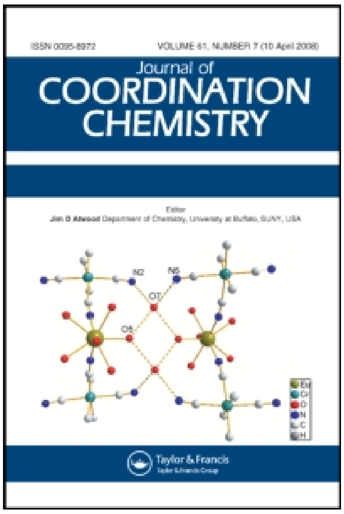

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CONTACT STABILIZATION OF HOST COMPLEX MOLECULES DURING CLATHRATE FORMATION: THE PYRIDINE-ZINC NITRATE AND THE PYRIDINE-CADMIUM NITRATE SYSTEMS

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CONTACT STABILIZATION OF HOST COMPLEX MOLECULES DURING CLATHRATE FORMATION: THE PYRIDINE–ZINC NITRATE AND THE PYRIDINE–CADMIUM NITRATE SYSTEMS*

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Clathrate formation ranges of the phase diagrams of two binary systems Py–$Zn(NO_3)_2$ and Py–$Cd(NO_3)_2$ (Py = pyridine) were studied. A clathrate of composition $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Zn, Cd) was observed in each of the systems. The space group *Ccca* (orthorhombic system) and the parameters of the unit cells of both clathrates were determined by X-ray analysis of their single crystals. The data obtained show them to be isostructural with the clathrate $[NiPy_4(NO_3)_2]\cdot 2Py$ whose structure is known and suggest the actual presence of the host molecules *trans*-$[MPy_4(NO_3)_2]$ (M = Zn,Cd) inside the clathrate phases. Host complexes do not form as separate compounds but can only arise in clathrate phases due to contact stabilization by the guest molecules. Both Zn- and Cd-clathrates are of constant composition and melt incongruently at 62.3(6) and 106.0(5)°C, respectively, yielding the complexes $[ZnPy_3(NO_3)_2]$ and $[CdPy_3(NO_3)_2]$, these melting congruently at 131.4(5) and 169.5(5)°C, respectively. During thermal decomposition under *quasi*-equilibrium conditions with different pressures of the liberating pyridine both clathrates also decompose in one stage, giving $[MPy_3(NO_3)_2]$ complexes. The results obtained are discussed in relation to a number of other systems with Schaeffer's and Hofmann-Iwamoto's clathrates in which contact stabilization occurs or might be expected to occur.

KEYWORDS: clathrate, phase diagram, contact stabilization, X-ray, metal(II), pyridine

INTRODUCTION

A complex molecule is attractive as a host because its dimensions and shape can be altered by the changing of the metal cation and the ligands added to the cation. This is the reason modification of coordination hosts as a way of obtaining clathrate phases with preset or unexpected properties is one of the main approaches used in the study of Hofmann-Iwamoto's,[1] Schaeffer's[2,3] and de Radzitzky's[4] clathrates.

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* This paper is dedicated to Professor T. Iwamoto

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This has been clearly demonstrated by lwamoto's and his colleagues' experiments on the purposeful modifying and designing of clathrate phases of new type. Substitution of bidentate ethylenediamine for monodentate ammonia in the classic Hofmann's compound[5-7] has made possible the formation of a three-diamensional host framework instead of the layered one.[8,9] This resulted in dramatic change of the phase properties (made it impossible to include guests with the dimensions exceeding a certain value) and has become the first step towards the creation of a large group of clathrate structures of new type whose metal cyanide sheets are rigidly bound to one another.[1,10-12] The changing of the rigidity and length of the diamine ligand and the introduction of bulky substituents into the ligand or substitution of 'tetrahedral' cations for 'square-planar' nickel cation made it possible to change the shape and size of the cavities in the host framework and thereby adjust the structure for the inclusion of a certain type of guests with a specified stoichiometry. Creation of new kinds of Werner's clathrates by systematic variation of neutral ligands in the host molecule was carried out by Nassimbeni *et al.*[13,14] and de Radzitzky *et al.*[4]

A supplementary approach consists in the study of the feedback, *i.e.*, the way a clathrate phase affects the coordination, conformation, and stability of a complex host molecule in general rather than investigation of the host molecule structural influence on the structure and properties of clathrates it forms. Cumulative contributions of weak van der Waals interactions in the overall phase stability multiplied by a great number of intermolecular contacts, can appreciably affect the parameters of molecules which make up the phase. If the host molecule is strong enough, like $[Ni(MePy)_4(NCS)_2]$ (MePy-4-methylpyridine), this influence shows both in regular changes of the lengths of the metal-ligand bonds[15], and in the conformation types;[3,16] the host molecule taking on the geometry which is most favorable for this clathrate structure. As the host stability decreases, influence of the contribution of non-valent interactions becomes increasingly prominent. In a limiting case the situation is observed where the host molecule itself is unstable (in this case the host compound as a separate phase does not exist), but it can arise inside the clathrate phase in the process of clathrate formation. This phenomenon was first observed in a number of clathrates with $[M(MePy)_4(NCS)_2]$ as a host and MePy as a guest and named 'contact stabilization of molecules'.[17,18]

While clathrates of $[MA_4X_2]$ complexes with substituted pyridines as the A-ligand whose investigation resulted in the discovery of this phenomenon have been studied rather well, clathrates of complexes with pyridine itself as the A-ligand are a new field. This complexes have recently been shown to form a large number of isostructural clathrates (orhorhombic, *Ccca*) of general formula $[MPy_4X_2]\cdot 2Py$ (Py - pyridine).[19] Clathrates with nitrate as X, and Zn and Cd as M are particularly interesting. Attempts to obtain $[MPy_4(NO_3)_2]$ complexes by decomposing these clathrates have not been successful,[20] no data on compounds of this composition can be found in the literature. This led us to believe that contact stabilization occurs in these systems.

EXPERIMENTAL

Pyridine (p.a.) used in the syntheses contained 0.25 mass% of water. To study the phase diagrams it was dried by distilling over freshly annealed BaO and kept over

Zeolite 3A (FERAK, Molekularsieb 0.3 nm., reinst). The resulting base contained not more than 0.02 mass% of water and melted at −43.2(4)°C.

The clathrate $[ZnPy_4(NO_3)_2]\cdot 2Py$ and the complexes $[ZnPy_3(NO_3)_2]$ and $[ZnPy_2(NO_3)_2]$ were obtained as crystals, using the procedure described in the literature.[21] The crystalline clathrate $[CdPy_4(NO_3)_2]\cdot 2Py$ and the complex $[CdPy_3(NO_3)_2]$ were obtained similarly. Determination of zinc, cadmium, and pyridine was carried out using literature techniques.[21,22] *Anal.* Calcd. for $[ZnPy_4(NO_3)_2]\cdot 2Py$ (%): Zn, 9.85; Py, 71.5. Found: Zn, 9.89(5); Py, 71.0(5). *Anal.* Calcd. for $[ZnPy_3(NO_3)_2]$ (%): Zn, 15.3; Py, 55.6. Found: Zn, 15.2(1); Py, 55.8(4). *Anal.* Calcd. for $[ZnPy_2(NO_3)_2]$ (%): Zn, 18.81; Py, 45.5. Found: Zn, 18.79(8); Py, 45.8(3). *Anal.* Calcd. for $[CdPy_4(NO_3)_2]\cdot 2Py$ (%): Cd, 15.8; Py, 66.8 Found: Cd, 15.7(1); Py, 66.5(5). *Anal.* Calcd. for $[CdPy_3(NO_3)_2]$ (%): Cd, 23.7; Py, 50.1. Found: Cd, 23.8(1); Py, 49.9(4).

Thermal decomposition processes were studied on a Q-derivatograph under *quasi*-equilibrium conditions[23] using different sample holders. The samples had a mass of *ca.* 150 mg, the rate of mass loss was 0.3 mg/min.

To determine the phase diagrams of the systems Py — $Zn(NO_3)_2$ and Py — $Cd(NO_3)_2$, DTA and solubility techniques were used. These procedures were described in detail earlier.[21,22] The diagrams were determined in the following ranges: for the Zn-system, −100/+150°C and 0/54.5 mass % $Zn(NO_3)_2$; for the Cd-system, − 50/ + 200°C and 0/60.0 mass % $Cd(NO_3)_2$.

The space group and the parameters of the unit cells of the clathrates $[ZnPy_4(NO_3)_2]\cdot 2Py$ and $[CdPy_4(NO_3)_2]\cdot 2Py$ were determined using a KM-4 single-crystal diffractometer (graphite-monochromatized MoK_α radiation, $\lambda = 0.7107$Å). Clathrate single crystals of size $0.3 \times 0.3 \times 0.5$ mm (Zn) and $0.3 \times 0.4 \times 0.5$ mm (Cd) were fixed inside Lindemann-glass capillary tubes filled with the corresponding mother liquor. An orthorhombic C-lattice was determined for each of the crystals on the basis of 25 reflections randomly chosen in the range $2\theta = 5/10°$. To test the symmetry found and to refine the unit cell parameters we used a random search and refinement of the location of the reflections in the range $2\theta = 20/35°$. The space group *Ccca* was determined for both clathrates on the basis of systematic absences observed during measurement of intensities of several dozen reflections.

RESULTS

The parameters of the unit cells of the studied clathrates and those of $[NiPy_4(NO_3)_2]\cdot 2Py$ studied earlier are listed in Table 1. All three compounds are isostructural.

Table 1 Some X-ray data on the $[MPy_4(NO_3)_2]\cdot 2Py$ clathrates (M = Zn, Cd, Ni).

Formula	Sp. group	*a*, Å	*b*, Å	*c*, Å	Ref.
$[ZnPy_4(NO_3)_2]\cdot 2Py$	*Ccca*	12.111(9)	15.11(1)	17.20(1)	this work
$[CdPy_4(NO_3)_2]\cdot 2Py$	*Ccca*	12.33(1)	15.47(4)	17.05(2)	this work
$[NiPy_4(NO_3)_2]\cdot 2Py$	*Ccca*	12.148(5)	15.019(4)	16.96(1)	24[a]

[a] Tentative data were reported at the Fourth International Summer School on Supramolecular Chemistry.[19]

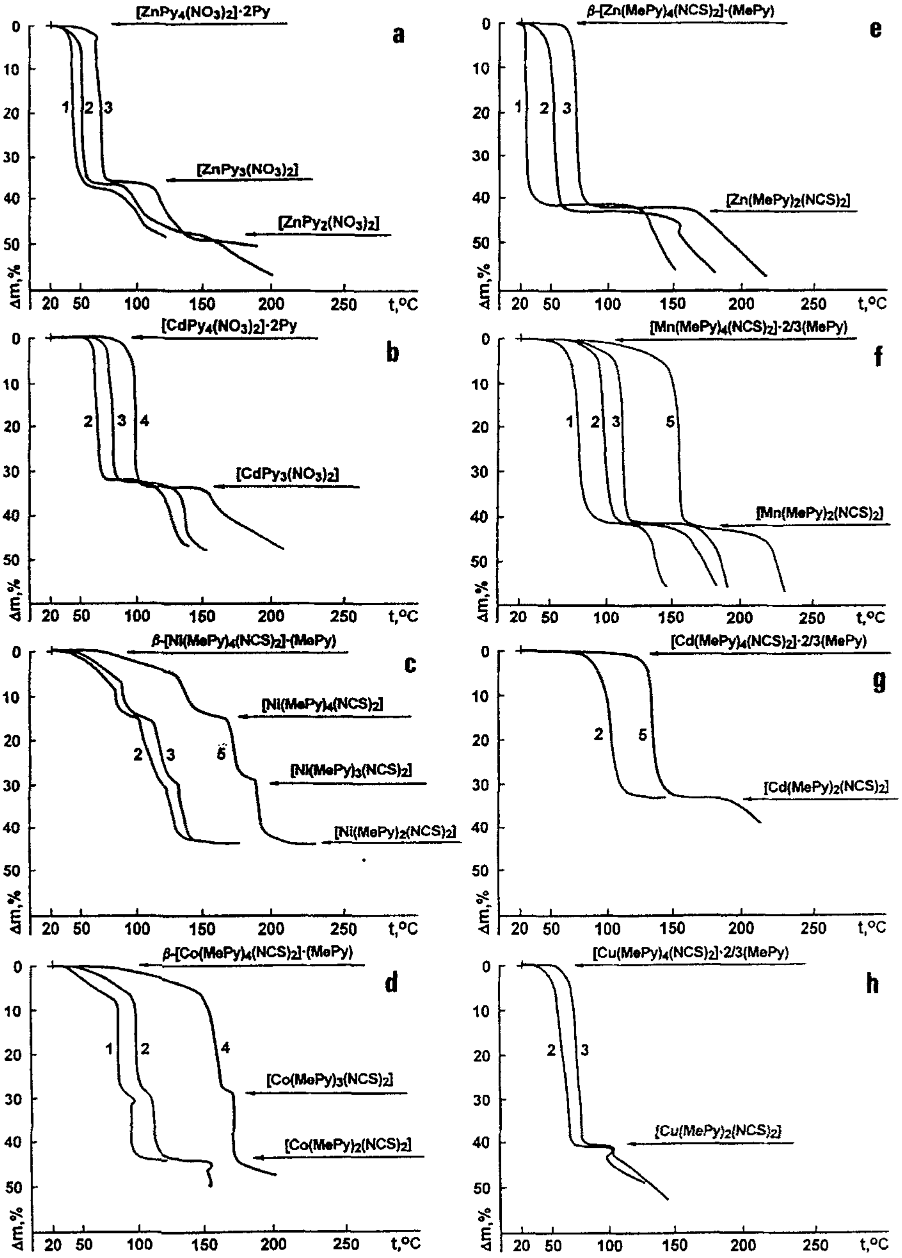

Figure 1 Thermal decomposition of the clathrates: a, $[ZnPy_4(NO_3)_2]\cdot 2Py$ (this work); b, $[CdPy_4(NO_3)_2]\cdot 2Py$ (this work); c, β-$[Ni(MePy_4(NCS)_2]\cdot(MePy)$[29]; d, β-$[Co(MePy_4(NCS)_2]\cdot(MePy)$[30]; e, β-$[Zn(MePy)_4(NCS)_2]\cdot(MePy)$[31]; f, $[Mn(MePy)_4(NCS)_2]\cdot 2/3(MePy)$[30]; g, $[Cd(MePy)_4(NCS)_2]\cdot 2/3\ (MePy)$[29]; h, $[Cu(MePy)_4(NCS)_2]\cdot 2/3(MePy)$[32]. Sample mass: 100–200 mg. Heating program: quasi-isothermal. Atmosphere: air. Sample holders: 1, plate crucible ($p = 0.01$ atm); 2, open ($p = 0.05$ atm); 3, covered ($p = 0.2$ atm); 4, conic ($p = 0.8$ atm); 5, labyrinth ($p = 1$ atm).

The mass loss curves of the clathrates for decomposition under *quasi*-equilibrium conditions are depicted in Fig.1 (a,b). The clathrates decompose to tripyridine complexes (M = Zn, Cd):

$$[MPy_4(NO_3)_2]\cdot 2Py \rightarrow [MPy_3(NO_3)_2] + 3Py\uparrow \qquad (1)$$

Changing the equilibrium pressure of the liberating pyridine does not cause any qualitative changes in the process. Comparison of the curves shows that the Zn-compound is less stable thermally than the Cd-compound in agreement with the data of the phase studies described below.

The phase diagrams of the studied systems in the range adjacent to pyridine are shown in Fig. 2. In the Py — $Zn(NO_3)_2$ system three compounds are observed in the temperature and composition interval. The clathrate $[ZnPy_4(NO_3)_2]\cdot 2Py$ melts incongruently at 62.3(6)°C according to the equation:

$$[ZnPy_4(NO_3)_2]\cdot 2Py \xrightarrow{62^\circ} [ZnPy_3(NO_3)_2] + \text{liquor} \qquad (2)$$

The compounds $[ZnPy_3(NO_3)_2]$ and $[ZnPy_2(NO_3)_2]$ melt congruently at 131.4(5) and 130.7(8)°C, respectively. In the Py — $Cd(NO_3)_2$ system a clathrate of the same composition is observed which melts incongruently at 106.0(5)°C as follows:

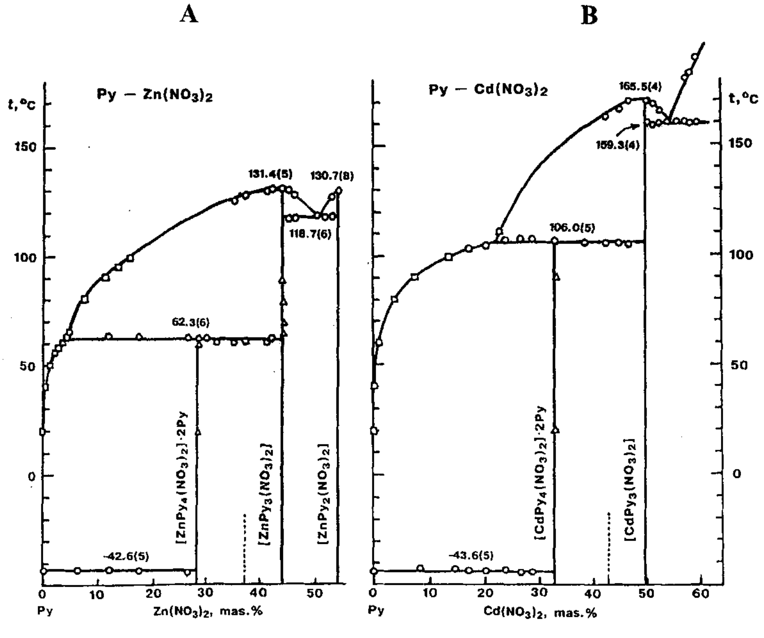

Figure 2 Phase diagrams of the clathrate formation ranges of the systems Py — $Zn(NO_3)_2$ (a) and Py = $Cd(NO_3)_2$ (b). Circles stand for the points obtained by the DTA technique; squares and triangles, for the points obtained by the analysis of the liquid and solid phases which are in equilibrium at a certain temperature, respectively. Dotted lines on both diagrams show the composition, which the host complex $[MPy_4(NO_3)_2]$ (M = Zn, Cd) would have.

$$[CdPy_4(NO_3)_2]\cdot 2Py \xrightarrow{106^\circ} [CdPy_3(NO_3)_2] + \text{liquor} \qquad (3)$$

The tripyridine complex $[CdPy_3(NO_3)_2]$ melts congruently at 169.5(4)°C; there is no dipyridine complex in this system.

It is obvious that these systems have common features: in both systems one can observe formation of a clathrate compound with the mole ratio host:guest = 1:2; the compounds melt incongruently according to Eq. **2** and **3**, yielding tripyridine complex phases. No phases of the host complexes $[MPy_4(NO_3)_2]$ are present in the systems. In both cases the eutectics Py(solid) + clathrate + liquor is degenerate, and its temperature coincides with the pyridine melting point (−43.2(4)°C) within experimental error. Thus, solubility of the clathrates below room temperature is quite low; and the equilibrium mother liquor over the clathrate crystals is actually pure pyridine. As the temperature approaches the peritectics, the solubility of clathrates rises steeply, especially for the Cd-compound. In both systems the clathrates are compounds of constant composition which is suggested both by the monovariant nature of their thermal decomposition under *quasi*-equilibrium conditions (Fig. 1a, b), and direct analysis of the equilibrium solid phase at various temperatures (triangles in Fig. 2). The main differences between the clathrate formation range diagrams of these systems are of quantitative nature and consist in much higher thermal stability of the corresponding compounds in the Cd-system.

DISCUSSION

The phase diagrams of the studied systems and the data of *quasi*-equilibrium thermogravimetry have led us to believe that although clathrate compounds[25] $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Zn, Cd) are observed in the systems, the phases of the corresponding host complexes $[MPy_4(NO_3)_2]$ do not form in the temperature ranges studied. The X-ray data unambiguously suggest the existence of the host molecules in the clathrate phases as is the case with the isostructural Ni-compound. The structure of the $[NiPy_4(NO_3)_2]$-molecule in the clathrate phase[24] is shown in Fig. 3. It is of *trans*-octahedral configuration with monodenate nitrate groups. The presence, in the studied clathrate phase, of the $[ZnPy_4(NO_3)_2]$-molecule of the same geometry as that in the Ni-compound was verified by spectral studies carried out by Nuttall *et al.*[26] Thus, the phenomenon of contact stabilization of the $[MPy_4(NO_3)_2]$-molecules (M = Zn, Cd) by the guest molecules does occur in phases of the studied clathrates.

The processes of decomposition of the $[MPy_4(NO_3)_2]\cdot 2Py$ clathrates in which pyridine liberates into the gaseous phase (Fig. 1a, b) and those of incongruent melting (Fig. 2) are identical, qualitatively, in the Zn- and Cd-systems. The influence of packing factors on decomposition of the Zn- and Cd-clathrates (Eq. **1–3**) should be practically the same because both the clathrates themselves (Table 1) and the resulting $[MPy_3(NO_3)_2]$ complexes[27,28] are isostructural. Therefore, the observed essential differences in stability of the clathrates should be determined by the stability differences between the $[ZnPy_4(NO_3)_2]$ and $[CdPy_4(NO_3)_2]$ host molecules with respect to their decomposition products, *i.e.*, tripyridine complexes and pyridine. Thus, it is the relative strength of the host molecule that determines the stability limits of its clathrate, with "the weak point" in reactions **1–3** being the coordination bond M-N_{Py}. Comparison of the studied systems with those in which the host stability changes in a wider range makes this conclusion more evident and better substantiated.

Fig. 1 shows the mass loss curves of the studied clathrates and those with $[M(MePy)_4(NCS)_2]$ as a host and MePy as a guest. These latter are of two structural types: the so-called β-clathrates with the host to guest ratio 1:1 (tetragonal, sp.gr. $I4_1/a$) and clathrates 1:2/3[33] (trigonal, sp.gr. $R\bar{3}$).

One can see that the nature of the decomposition of β-clathrates strongly depends on the metal cation (Fig. 1c, d, e). In the case of the Ni-clathrate, the host complex is quite stable and it always shows distinctly as a step on the mass loss curves. The Co-clathrate decomposes in one stage without a host phase as an intermediate giving the *tris* (MePy)-complex. Lower strength of the Co-host results in a decrease of the thermal stability of its clathrate. Finally, in the case of Zn-clathrate, where there is no host compound at all,[22] the decomposition occurs at much lower tempheratures and in one stage, resulting in *bis*(MePy)-complex. It is notable that although the clathrates $[ZnPy_4(NO_3)_2]\cdot 2Py$ and β-$[Zn(MePy)_4(NCS)_2]\cdot(MePy)$ are similar only in the presence of Zn-N (ligand of pyridine type) bonds and in the absence of the separate host, their decomposition temperatures are almost the same whether decomposition occurs with formation of gaseous and solid phases (Fig. 1a, e) or with liquid and solid ones (Fig. 2a and 4d).

The decomposition of all three trigonal clathrates (Fig. 1f, g, h) occurs in a similar way, in one stage with formation of *bis*(MePy)-complexes, but their decomposition temperatures differ markedly, depending on the host molecule cation. The clathrate $[Cu(MePy)_4(NCS)_2]\cdot 2/3(MePy)$ whose host compound does not exist at all[34] is the least stable. The decomposition temperatures of $[Cd(MePy)_4(NCS)_2]\cdot 2/3(MePy)$ are significantly higher since in this case the host is stable enough to exist as a separate phase.[35,36]

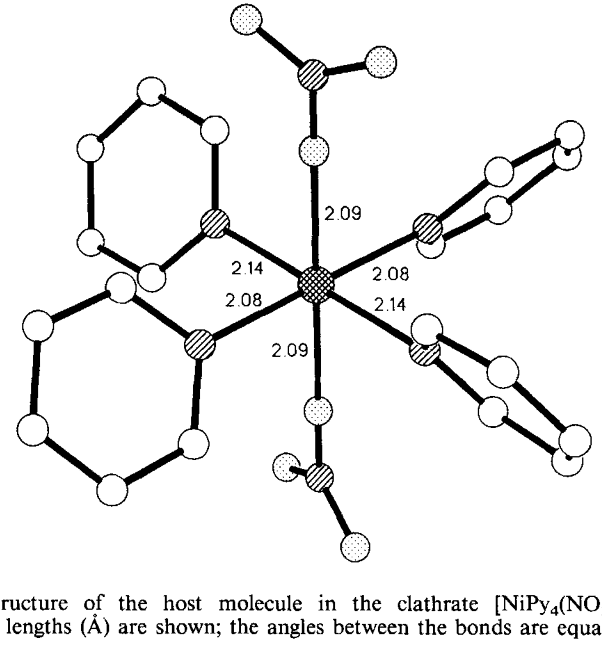

Figure 3 The structure of the host molecule in the clathrate $[NiPy_4(NO_3)_2]\cdot 2Py$[19,24]. The metal-ligand bond lengths (Å) are shown; the angles between the bonds are equal to 90°.

Especially illustrative is comparison of the phase diagrams of the MePy — $M(SCN)_2$ systems in clathrate formation ranges[37] (Fig. 4). In the Ni-system the host complex is stable up to 209°C; up to 150°C the clathrate stability is determined by interactions among molecules, rather than the strength of the host molecule. In this system the clathrate matrix of the host (β-phase) is retained on guest removal; and a limited field of solid solutions forms on the basis of the clathrate structure (the clathrate phase remains thermodynamically stable when up to 30% of the guest is removed in water solution at 25°C[39]). In the Cd-system the situation reverses dramatically; the clathrate decomposes at a temperature 5°C higher than does the host. The coordination host molecules thus exist within the clathrate phase in the temperature range 134–139°C where they cannot exist as a separate phase. In other words, in this clathrate phase non-valent interactions favor the existence of the host molecule. In the Cu- and Zn-systems the host does not form its own compound, but its molecules do form and actually exist in the clathrate phase. In the systems concerned decrease of the host stability is accompanied by decrease of the stability of the clathrates it forms. However, the stability of the clathrates decreases much slower due to the stabilization of the coordination host molecule by non-valent interactions when the host and the guest molecules are packed together. When the host is highly stable (Ni-system), destruction of the clathrate is caused by guest removal while the host molecules are retained. In the case where the host is absolutely unstable outside the clathrate of the Cu- or Zn-systems, clathrate decomposition is caused by decomposition of the host. Measurements of the temperature dependence of MePy vapor pressure over the clathrates $\beta\text{-}[Ni(MePy)_4(NCS)_2]\cdot y(MePy)$ and $\beta\text{-}[Zn(MePy)_4(NCS)_2]\cdot(MePy)$[31] show that the former is a solid solution with a variable host to guest ratio (y changes from a certain value to 1), while the latter is a constant composition compound with stoichiometry corresponding to complete filling of the host matrix cavities with guest molecules. Instability of the clathrate host framework caused by guest removal might be due to two reasons: either instability of the structure (unfavorable spatial arrangement of the host molecules which in the absence of the guest rearrange into a different structure) or instability of the molecules themselves.[18] The fact that in the Ni-system the host β-framework is stable and can persist even after complete guest removal (as a metastable phase)[41,45] indicates that the host molecules in the β-phases arrange quite advantageously. Therefore, decomposition of the β-clathrate in the Zn-system is brought about by instability of the host molecules themselves rather than unfavorable spatial arrangement of these molecules. In the clathrate phase this molecule is supported externally with the power of non-valent interactions and breaks down with splitting off the ligands as soon as this outside support decreases or disappears.

The latter situation presents the essence of contact stabilization phenomena. In this case one could consider that the clathrate phase contains host fragments rather than entire host molecules. Coordination bonds connecting the host fragments contribute to the structure stability, but these bonds alone are not sufficient. Regardless of the ability of the coordination molecule to exist which was discussed above, its geometry and the character of ligand coordination in this case strongly depend on non-valent interactions available within one or other clathrate structural type. The most impressive illustration of this dependence comes from comparison of the $[Cu(MePy)_4(NCS)_2]$ host molecules in two clathrates of the host with MePy as a guest: the blue one (monoclinic, mole host:guest ratio 1:2)[17,18,44] and the green

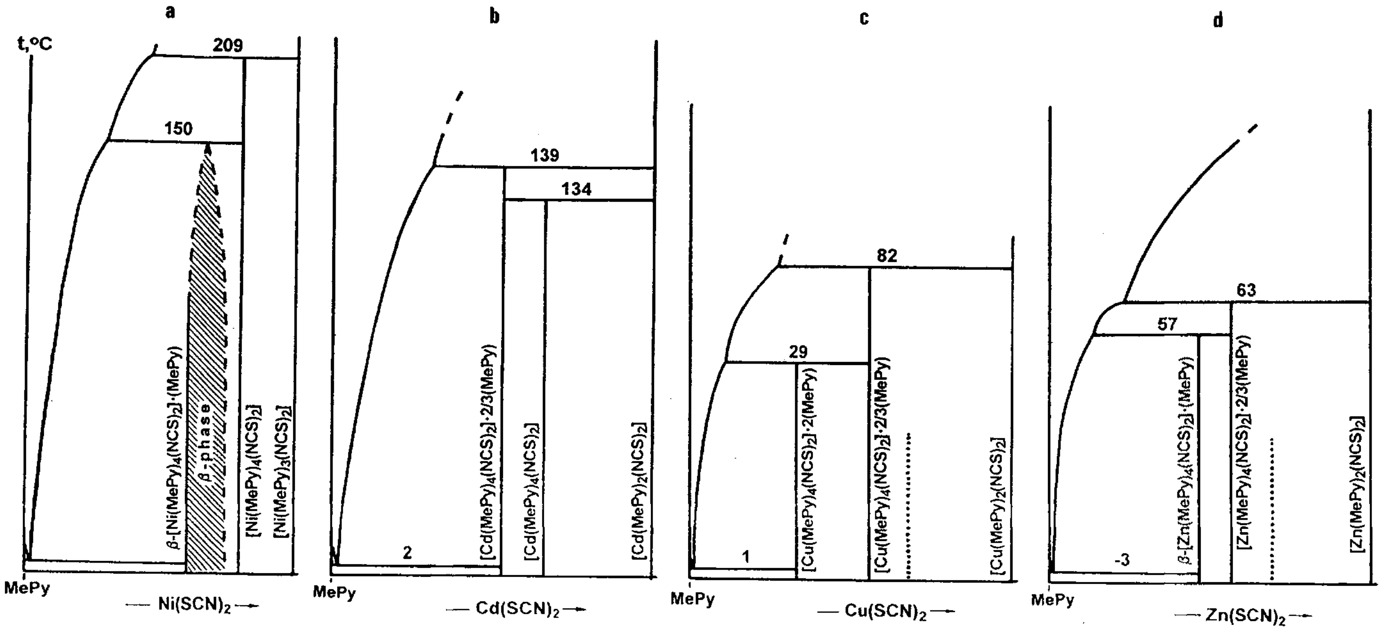

Figure 4 The phase diagrams of the systems MePy — $M(SCN)_2$ in clathrate formation ranges (schemes): a, Ni-system[38]; b, Cd-system[35,36]; c, Cu-system[17,34,44]; d, Zn-system[17,22].

one (trigonal, 1:2/3)[17,18,46] (Fig. 5). Even the difference in colour between these compounds alone, which in both cases depends on host molecules of composition $[Cu(MePy)_4(NCS)_2]$ points to dramatic differences in their structure. In the 1:2 clathrate the coordination octahedron of Cu(II) is distorted due to substantial elongation of the bonds $Cu\text{-}N_{CS}$ (Fig. 5a), so that isothiocyanate ligands become weakly connected and are practically packed in the structure in the form of ions. This is suggested by the $Cu\text{-}N_{CS}$ distance and the position of the absorption band

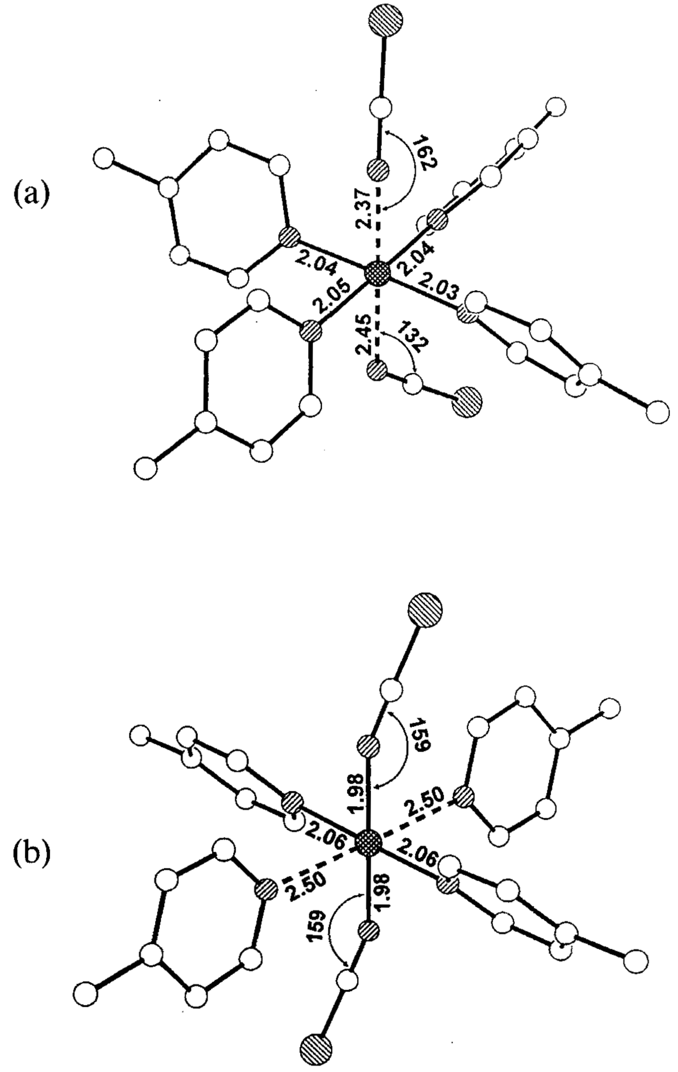

Figure 5 The structure of the host complex molecule in the blue clathrate $[Cu(MePy)_4(NCS)_2]\cdot 2(MePy)$[44] (a) and the green clathrate $[Cu(MePy)_4(NCS)_2]\cdot 2/3(MePy)$[46] (b). The bond lengths (Å) and some of the angles (°) are shown.

$\nu(CN) = 2043\ cm^{-1}$ in the IR-spectrum[47] typical of the thiocyanate ion. In the 1:2/3 clathrate the octahedron is also substantially distorted, but this is due to elongation of the bonds between Cu(II) and two MePy ligands, while the bond between Cu(II) and the nitrogen of the isothiocyanate group is almost 0.5 Å shorter than that in the 1:2 clathrate. Therefore, $\nu(CN) = 2090\ cm^{-1}$ which corresponds to the NCS-group coordinated by nitrogen.[47]

Understanding of the contact stabilization phenomenon was one of the starting points for this study. It precluded the conventional procedure including the previous synthesis of the host compound. Extension of the regularities found for the MePy—$M(SCN)_2$ systems to the Py—$M(NO_3)_2$ systems proved successful. Systems where the number of components exceeds two are less aminable to a sophisticated phase study. However, even in this case it is useful to predict whether or not obtaining in the clathrate phase of the molecules of the complex, which does not exist as a separate phase, is possible. In most cases the stage of previous host synthesis is omitted from the procedure for obtaining Hofmann-Iwamoto's clathrates. It seems likely that, in many of these compounds, contact stabilization of planar-polymer host molecules by the included guest species also occurs. "The weak point" of the polymer host molecules in these clathrates as well as in Schaeffer's clathrates discussed above is the coordination bond between the metal(II) cation and the nitrogen atom of the amine or diamine ligand. For instance, during thermal decomposition of the clathrates $[M(NH_3)_2Ni(CN_4]\cdot 2(C_6H_6)$ and $[M(NH_3)_2 Pd(CN)_4]\cdot 2(C_6H_6)$ (M is metal(II) coordinated octahedrally by six nitrogen atoms) the guest benzene is removed without host decomposition only in the case of M = Ni; when M = Cd, Cu removal of the guest is accompanied by partial dissociation of the host with the cleavage of the amine ligands.[48] Therefore, under these conditions the host might be supposed to be unstable in the absence of the guest. It seems likely that the host component would not be able to exist with the structure it would have in the clathrate, because it would be too porous. On the other hand, with octahedrally directed M(II) bonds and the available set of ligands the building of a sufficiently dense modification is not possible. In this connection it would be interesting to recall observations of Iwamoto *et al.*, on changing of the host $[Cd(NH_3)_2Ni(CN)_4]$ clathrate formation ability caused by substitution of methyl substituted analogues of the ammine ligand.[1] With ammine, monomethylamine, and dimethylamine ligands the mole host to guest ratios in the majority of the forming clathrates are 1:2, 1:3/2, and 1:1, respectively while the complex with the trimethylamine ligand does not produce any clathrates.[49] In this series the methyl moiethies of the host fill the empty space in the clathrate framework successively, resulting in decrease of the amount of the guest, required to create a dense phase and thus stabilize the available host structure. In the latter case contact stabilization of the host by the guest is not required since bulky trimethylamine ligands tightly fill the empty space between polymeric metal cyanide sheets and seem to play the part of the guest. In this case the host "stabilizes" itself.

From the above discussion it follows that, in some of the systems, non-valent interactions can play an important or even a crucial role. Although the energy of a chemical bond is much higher than that of any intermolecular interaction, in the case where the difference in the free energy between the host complex and its decomposition products is small, non-valent interactions can determine the direction of a chemical reaction. This allows chemists to create and study new coordination compounds which cannot be obtained as separate phases by their stabilization within a clathrate structural type.

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References and Notes

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