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Clathrate Formation and Phase Equilibria in the Pyridine–Cadmium Nitrate System

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Abstract. Preparative, thermal (DTA, TGA), solubility, strain and spectral (Raman) techniques were used to study clathrate and complex formation in the pyridine (Py)–cadmium nitrate system. Three compounds have been isolated and studied: the clathrate compound $[CdPy_4(NO_3)_2] \cdot 2Py$ (**I**), the complex $[CdPy_3(NO_3)_2]$ (**II**) and a compound of composition 'Cd(NO$_3$)$_2$·7/4Py' (**III**), of unknown nature. The phase diagram of the system has been determined for the concentration and temperature range 0–66 mass-% Cd(NO$_3$)$_2$ and -100 to $+200$ °C, respectively. Clathrate **I** undergoes polymorphous conversion at $-51.8(4)$ °C and melts incongruently at $106.0(5)$ °C, forming complex **II**. Compounds **II** and **III** melt congruently at $165.5(4)$ and $191(1)$ °C, respectively. The complexes $[CdPy_4(NO_3)_2]$ (the host phase) and $[CdPy_2(NO_3)_2]$ are not observed in the system. The nature and thermodynamic parameters of the dissociation of clathrate **I** have been determined. For the process $1/3[CdPy_4(NO_3)_2] \cdot 2Py_{solid} = 1/3[CdPy_3(NO_3)_2]_{solid} + Py_{gas}$ in the range 290–360 K $\Delta H° = 54.9(3)$ kJ/mole, $\Delta S°_{298} = 142(1)$ J/(mole K), $\Delta G°_{298} = 12.5(5)$ kJ/mole.

Key words: phase diagram, vapour pressure, thermal analysis, clathrate, pyridine.

1. Introduction

The formation of supramolecular compounds in pyridine–metal(II) salt systems was unexpected for two reasons [1–3]. First, many of these compounds of composition $[MPy_4X_2] \cdot 2Py$ (M = metal(II); Py = pyridine, C_5H_5N; X = univalent acidoligand) were discovered long ago, but until recently were referred to as 'hexapyridine–metal complexes $[MPy_6]X_2$'. Second, structurally, they seemed to be similar to the so-called Schaeffer's clathrates [4] formed by the host complexes *trans*-$[MA_4X_2]$ where 39 different substituted pyridine bases, but not pyridine itself, acted as a neutral ligand A [5, 6]. This is why it was believed that pyridine complexes cannot form clathrates at all [6].

The pyridine – M(NO$_3$)$_2$ systems (M = Cd, Co, Ni, Zn), in which clathrates $[MPy_4(NO_3)_2]$·2Py form, are of particular interest because the corresponding $[MPy_4(NO_3)_2]$ host complexes cannot be found in the literature. The phenomenon of contact stabilization of the host molecules in clathrate structures [7, 8] discovered in this kind of system suggests that these host complexes are not stable as separate compounds. Indeed, detailed study of the phase equilibria in the

pyridine–zinc nitrate system has verified the absence of the host stability range in this system [9]. Now the results of our investigations on the pyridine–cadmium nitrate system are reported.

The techniques used that allow qualitative and quantitative descriptions of the phase and structural changes in similar systems have been successfully applied before to study clathrates and clathrate formation processes, including determination of the phase diagrams of binary systems with clathrate formation [8–10], elucidation of the mechanisms of thermal decomposition of clathrates under quasi-equilibrium conditions [11, 12], finding the thermodynamic parameters of clathrate formation processes on the basis of the P–T relationships [13–15], and structural study of the host and guest subsystems in clathrate frameworks by means of Raman spectroscopy [16–18].

2. Experimental

2.1. PREPARATIONS

Pyridine (p.a.) used in the syntheses contained 0.25 mass-% of water. When needed (to prepare samples for strain measurements, for the phase diagram study etc.) it was additionally dried by distilling over BaO [21] and kept over zeolite 3A ('reinst'). The resulting reagent contained 0.017(2) mass-% of water and melted at $-(43.6-42.8)\,^\circ C$ (cf. literature data, $-42.7\,^\circ C$ [19]). (Here and below given in the brackets are standard deviations in the units of the last meaningful figure.)

Cd(NO$_3$)$_2$·4H$_2$O (p.a.), chloroform ('medical') and benzene (p.a.) were not additionally purified.

2.1.1. [CdPy$_4$(NO$_3$)$_2$]·2Py, dinitratotetrakis(pyridine)cadmium(II)–pyridine clathrate (1 : 2)

Cd(NO$_3$)$_2$·4H$_2$O (30.4 g: 0.1 mole) was dissolved by heating in 65 mL of pyridine. After cooling the clathrate crystals were separated on a glass filter and dried in flowing air until they decomposed completely (for 1–2 days). The powdery complex [CdPy$_3$(NO$_3$)$_2$] obtained was recrystallized from the dried pyridine (3 mL of pyridine per gram of the complex). *Anal. Calcd.* for [CdPy$_4$(NO$_3$)$_2$]·2Py (%): Cd, 15.8; Py, 66.8. *Found* Cd, 15.7(1); Py, 66.5(5). Yield on cadmium nitrate: 90%.

The powdery clathrate was obtained following the procedure described in Ref. [20] by placing [CdPy$_3$(NO$_3$)$_2$] into a desiccator under pyridine vapour. The increase of mass corresponded to 3.15 moles of pyridine per mole of initial complex.

2.1.2. [CdPy₃(NO₃)₂], dinitratotris(pyridine)cadmium(II)

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The powdery complex obtained by the above procedure was purified by salting out with a yield of 80%. The complex (19 g: 0.04 mole) was dissolved in a mixture of 115 mL of chloroform and 0.3 mL of the dried pyridine. Benzene (80 mL) was added to the hot stirred solution over 15 minutes, the heating was then stopped and the solution stirred for an hour. Fine crystals of the complex were separated on a glass filter and dried in air. *Anal. Calcd.* for [CdPy$_3$(NO$_3$)$_2$] (%): Cd, 18.81; Py, 45.5. *Found* Cd, 18.79(8); Py, 45.8(3).

Both compounds are well soluble in water, but not hygroscopic. The analysis showed that they did not contain water.

2.1.3. Cd(NO₃)₂·7/4Py

2.1.3. Cd(NO$_3$)$_2$·7/4Py

This compound was obtained by thermal decomposition of 400 mg of the complex [CdPy$_3$(NO$_3$)$_2$] under quasi-equilibrium conditions (open crucible). The heating was stopped after the sample lost 20.6% of its original mass and the TGA curve became horizontal (cf. Figure 3). *Anal. Calcd.* for 'Cd(NO$_3$)$_2$·7/4Py' (%): NO$_3$, 33.08. *Found:* NO$_3$, 33.01(7). The compound is soluble in water. However, its product resulting from further calcination when dissolved in water produces insoluble residue.

2.2. METHODS

Cd was determined by titration with 0.05M EDTA solution, using eriochrome black T as an indicator; pyridine, potentiometrically by reverse titration with 0.4M KOH solution of the excess of 0.4M nitric acid remaining after the neutralization of the base; water, following the Karl Fisher technique with visual endpoint detection. Gravimetric determination of nitrate was carried out by precipitating the complex with nitron. The technique used to handle crystals of compounds that are unstable in air was described in Refs. [8, 9].

To study the phase diagram, DTA (the samples were examined in closed ampoules) and solubility techniques were used, which have been described in detail in Refs. [8, 9]. The system was studied in the concentration and temperature ranges 0–66 mass-% Cd(NO$_3$)$_2$ and -100 to $+200$ °C, respectively. No significant kinetic complications were observed in the system. It should be mentioned that crystallization of the clathrate from saturated solutions is often delayed by several minutes.

Raman spectra were recorded with a Spex Triplemate Raman spectrometer. The spectra were excited with the 488 nm line of an Ar$^+$ laser and recorded with a multiscan detector O-SMA. A powdery clathrate sample was sealed in a thin-wall glass ampoule and placed in a cold-carrier of an optical cryostat with regulated temperature, LT-110K module from APD-Cryogenics (England). The accuracy of

the temperature of the cold-carrier was ±0.1 °C; the temperature of the sample could rise to some extent (2–3°) during the experiment.

Thermal decomposition processes were studied by the TGA technique on a MOM Q-1500-D derivatograph (Hungary) under quasi-isobaric, quasi-isothermal conditions, using various types of standard sample holders [21]. The crucibles used provided the following pressure values of the reaction gas product: 0.05 (open crucible), 0.20 (closed one) and 0.80 atm. (conic one). The mass of the samples was 150 mg, and the speed of the mass loss was 0.3 mg/min.

In strain experiments, pressure was measured by the static method, using a glass membrane null-manometer [13]. Two sets of measurements were carried out in the range 290–360 K. They differed in cadmium nitrate to pyridine ratio in the system studied. In the first series, 400 mg of the clathrate $[CdPy_4(NO_3)_2]\cdot 2Py$ powder was taken; the reaction vessel (ca. 40 mL) with the sample was evacuated for some time to remove the air and the excess pyridine adsorbed by the sample, and then sealed. Before the beginning of the second series of measurements, 20 mg of pyridine from the above sample was frozen out into a side vessel via the gaseous phase (the volume of the side vessel did not exceed 1 mL), and sealed off (22% of the initial amount of the guest or 0.45 moles of pyridine per clathrate mole). The equilibrium pressure over the clathrate was established practically at the same time as the required temperature was achieved, both in the forward and backward directions.

3. Results and Discussion

3.1. PHASE DIAGRAM AND COMPOUNDS OF THE SYSTEM

In the temperature and composition range of the system studied, three compounds are observed: the clathrate $[CdPy_4(NO_3)_2]\cdot 2Py$, the complex $[CdPy_3(NO_3)_2]$ and a compound of composition '$Cd(NO_3)_2\cdot 7/4Py$'. The first two substances were obtained as individual crystalline phases; the third one was obtained as a powder by the quasi-equilibrium thermogravimetric technique (see below). When exposed to air the clathrate crystals decompose, losing three pyridine moles. Placed into a desiccator under pyridine vapour the resulting powdery $[CdPy_3(NO_3)_2]$ absorbs about three pyridine moles once again. The process can thus readily go in the reverse direction.

The phase diagram is shown in Figure 1, and the coordinates of the liquidus curve experimental points in Table I. The eutectics Py_{solid} + $[CdPy_4(NO_3)_2]\cdot 2Py_{solid}$ = liquor is degenerate and its temperature practically coincides with the pyridine melting point. The clathrate solubility is rather low at room temperature, but increases sharply on heating. At 106.0(5) °C the clathrate melts incongruently according to the equation:
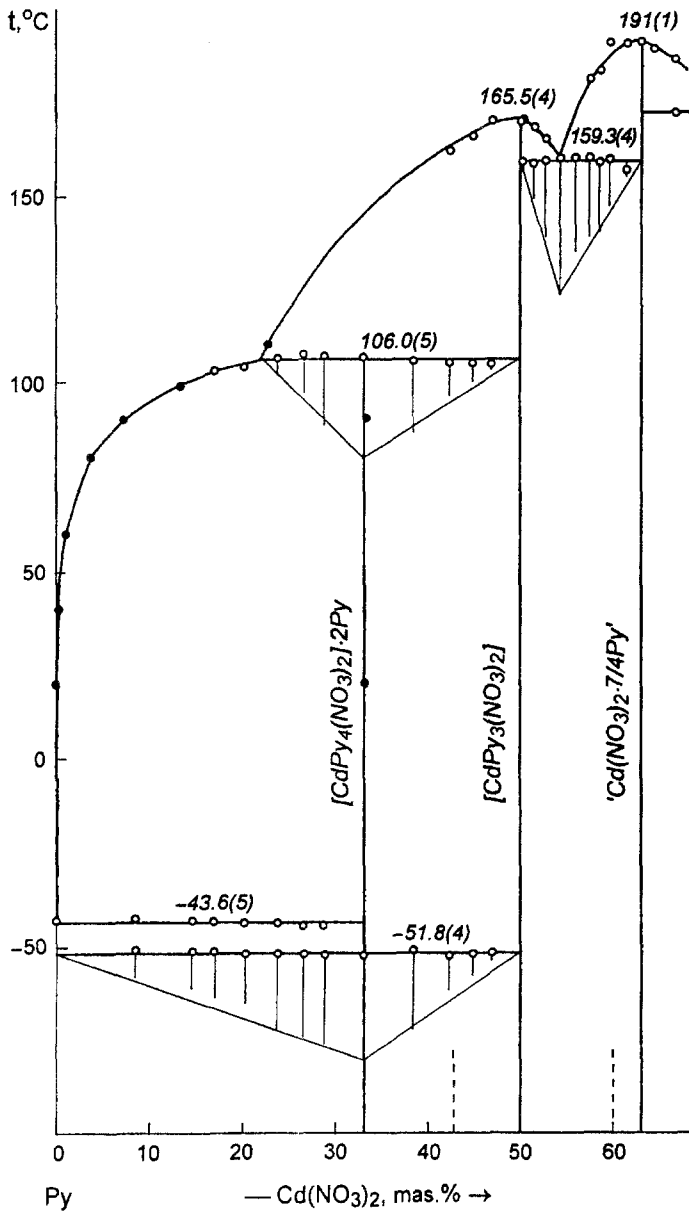
$$[CdPy_4(NO_3)_2]\cdot 2Py_{solid} = [CdPy_3(NO_3)_2]_{solid} + liquor \qquad (1)$$
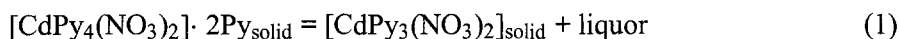
Figure 1. The phase diagram of the pyridine–cadmium nitrate system in the range studied. Open and solid circles represent the points obtained by the DTA and solubility methods, respectively. Dashes show the compositions, which the complexes [CdPy$_4$(NO$_3$)$_2$] and [CdPy$_2$(NO$_3$)$_2$] would have. For clarity the magnitudes of polymorphous thermal effects are enlarged ten times relative to the magnitudes of the remaining phase transition effects.

Table I. Coordinates of the liquidus curve experimental points in the system pyridine–cadmium nitrate

$Cd(NO_3)_2$, mass-%	t, °C	Method	Solid phase in equilibrium
0	−43.2(4)	DTA	Py (solid)
0.063(6)	20.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py^*$
0.25(1)	40.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py$
0.98(1)	60.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py$
3.68(4)	80.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py$
7.24(4)	90.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py^{**}$
13.25(8)	99.0	Solubility	$[CdPy_4(NO_3)_2] \cdot 2Py$
16.9	103	DTA	$[CdPy_4(NO_3)_2] \cdot 2Py$
20.2	104	DTA	$[CdPy_4(NO_3)_2] \cdot 2Py$
22.7(1)	110.0	Solubility	$[CdPy_3(NO_3)_2]$
42.3	162	DTA	$[CdPy_3(NO_3)_2]$
44.8	166	DTA	$[CdPy_3(NO_3)_2]$
46.8	170	DTA	$[CdPy_3(NO_3)_2]$
49.9	169.5(4)	DTA	$[CdPy_3(NO_3)_2]^{***}$
50.1	170	DTA	$[CdPy_3(NO_3)_2]$
51.4	168	DTA	$[CdPy_3(NO_3)_2]$
52.6	165	DTA	$[CdPy_3(NO_3)_2]$
57.5	181	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'
58.5	183	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'
59.6	191	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'
61.4	191	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'
62.9	191(1)	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'***
64.3	189	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'
66.8	186	DTA	'Cd$(NO_3)_2 \cdot 7/4$Py'

* *Anal* Cd: *found*, 15.8(1); *calcd.*, 15.8.
** *Anal* Cd: *found*, 15.9(1); *calcd.*, 15.8.
*** Distectic point.

The complex $[CdPy_3(NO_3)_2]$ and compound 'Cd$(NO_3)_2 \cdot 7/4$Py' melt congruently at 165.5(4) and 191(1) °C, respectively.

At −51.8(4) °C (221 K) a phase transition is observed in the system. The corresponding thermal effect is weaker than the effects of other transformations by one order and its maximum occurs on the clathrate composition (Figure 1). Figure 2 shows low- and some high-frequency fragments of Raman spectra of the clathrate sample at temperatures 150–290 K. Crystalline (123 cm^{-1}) and intramolecular modes of the pyridine host and guest moieties (1013, ca. 1044 cm^{-1}, etc. and 994, 1034 cm^{-1}, etc., respectively) practically do not change their frequency and intensity values in the temperature range concerned. This rules out the decomposition of the clathrate below the transfer point into solid pyridine and the complex $[CdPy_3(NO_3)_2]$ (decomposition of an 'endothermic' compound [22]). However,

the band at ca. 214 cm^{-1}disappears completely in the range 210–220 K. This frequency is likely to be characteristic of the oscillations of the M—O_{NO_2} bond. A jump-wise decrease of the intensity of the asymmetrical modes of the anion NO_3^- valent vibrations (1315, 1422 cm^{-1}) is observed in the same temperature range. Therefore, the observed phase transition has to do with the condition of the nitrate group in the host subsystem and its bonding with the cadmium cation, while the clathrate framework and composition do not change. Thus, the phase transition under consideration is a polymorphous transformation of the [CdPy$_4$(NO$_3$)$_2$]·2Py clathrate.

As is seen from Figure 1, no phases of the complexes [CdPy$_4$(NO$_3$)$_2$] (host) and [CdPy$_2$(NO$_3$)$_2$] are observed in the temperature range studied. This accounts for the absence of literature data on these compounds, while [CdPy$_4$(NO$_3$)$_2$]·2Py and [CdPy$_3$(NO$_3$)$_2$] occurring in the system have not only been described, but also studied structurally [3, 23].

In general, the clathrate formation part of the diagram is similar to that of the pyridine-zinc nitrate system [9]; the differences are mainly quantitative and consist of the higher thermal stability of the corresponding Cd compounds. Obviously, this is due to different strengths of metal–ligand coordination bonds in the analogous Zn- and Cd-compounds, which are isostructural [3, 23, 24]. This interesting situation, where marked differences in clathrate stability are due to the stability of the host itself rather than differences in the host–guest interactions, is quite characteristic of systems with complex host components.

3.2. THERMAL DISSOCIATION OF THE COMPOUNDS

Analysis of the mass loss due to the decomposition of the clathrate [CdPy$_4$(NO$_3$)$_2$]· 2Py under quasi-isobaric, quasi-isothermal heating conditions (Figure 3) indicates that a change in pressure of the evolving pyridine does not cause any changes in the manner of the clathrate decomposition, which follows the reaction:

$$[CdPy_4(NO_3)_2]\cdot 2Py_{solid} = [CdPy_3(NO_3)_2]_{solid} + 3Py_{gas} \qquad (2)$$
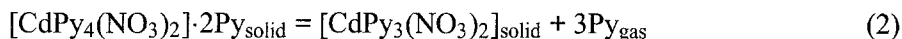
i.e. the clathrate phase decomposition is accompanied by breakdown of the host complex [CdPy$_4$(NO$_3$)$_2$].

The data on the temperature dependence of the pyridine vapour pressure in the process of clathrate dissociation for both series of the strain experiment coincide within the limits of the scatter caused by the experimental error of measurement. (Analysis of the distribution of the deviations was carried out as in Ref. [13].) They have been treated using the least squares technique and in the temperature range under investigation (290–360 K) are described by the equation:

$$\log P = (10.30 \pm 0.06) - (2866 \pm 18)/T \quad \text{(27 experimental points)}$$

This dependence and the experimental data are presented in Figure 4. (Here, in Figure 4 and Equation (3) pressure is given in torr (1 torr = 133.322 Pa) and temperature in Kelvins.) The type of the relationship shows that the studied equilibrium
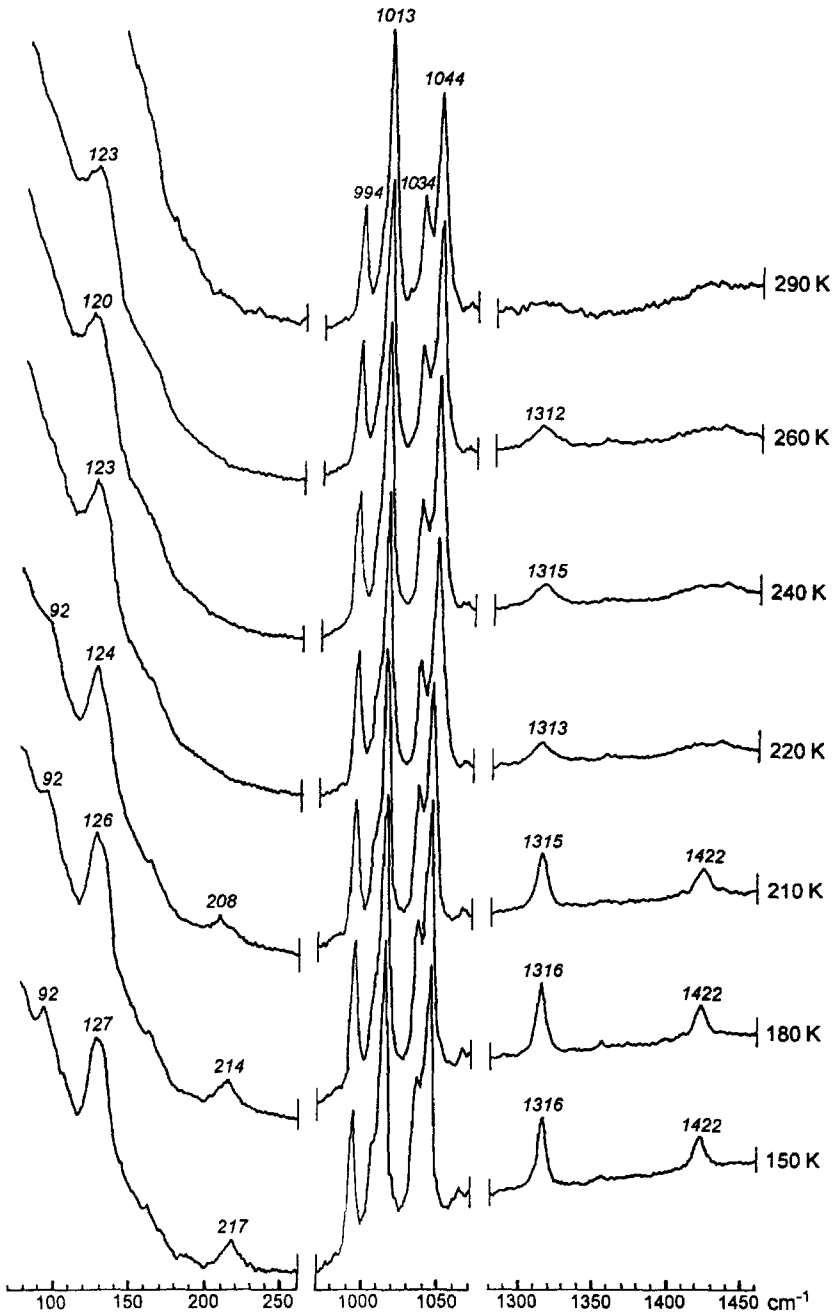
Figure 2. Raman spectra of the clathrate $[CdPy_4(NO_3)_2]\cdot2Py$ at different temperatures (selected fragments).

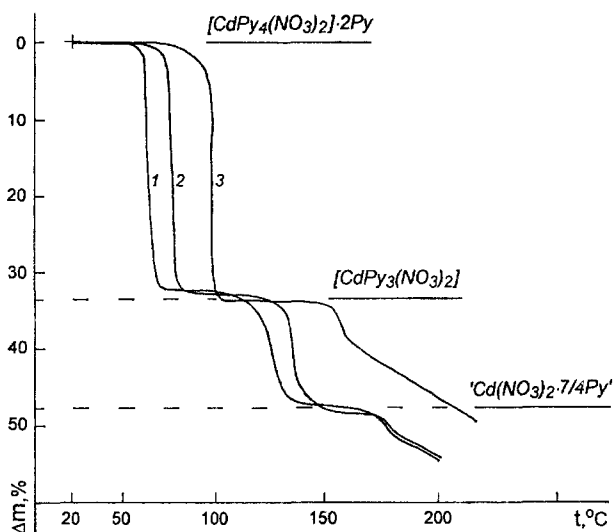*Figure 3.* Mass loss curves for the clathrate [CdPy$_4$(NO$_3$)$_2$]·2Py; heating program: quasi-isothermal; q = 0.3 mg/min; sample holders: 1, open; 2, covered; 3, conic crucibles.

Table II. Thermodynamic characteristics of the processes 1/3[CdPy$_4$(NO$_3$)$_2$]·2Py$_{solid}$ = 1/3[CdPy$_3$(NO$_3$)$_2$]$_{solid}$ + Py$_{gas}$ (A) and Py$_{liquid}$ = Py$_{gas}$ (B)

Process	Temperature range, K	$\Delta H°$, kJ/mole	$\Delta S°_{298}$, J/(mole K)	$\Delta G°_{298}$, kJ/mole	Ref.
A	290 ÷ 360	54.86 ± 0.34	142.0 ± 1.1	12.52 ± 0.47	This work
B	289 ÷ 358	39.33 ± 0.19	101.9 ± 0.6	8.95 ± 0.26	[25]

is monovariant, and according to Equation (2) three phases are in equilibrium: the solid clathrate [CdPy$_4$(NO$_3$)$_2$]·2Py, the solid complex [CdPy$_3$(NO$_3$)$_2$] and gaseous pyridine. The enthalpy, standard entropy and isobaric–isothermal potential of the clathrate dissociation process, based on this relationship, are presented in Table II. Comparing them with the parameters of the evaporation process of pyridine, one can easily obtain parameters of the clathrate dissociation process yielding liquid pyridine, e.g. $\Delta H°$ = 46.6 ± 1.6 kJ/(mole of clathrate). In fact they are characteristic of process (1) under standard conditions given the low clathrate solubility at room temperature (Table I).

Decomposition of the complex [CdPy$_3$(NO$_3$)$_2$] is due to further loss of about 1.25 moles of pyridine (Figure 3). The resulting compound, corresponding to steps on the mass loss curves, was extracted and studied. Weight determination of nitrate content in the product (33.01(7) mass-% NO$_3$) allowed us to assign the empirical formula 'Cd(NO$_3$)$_2$·1.76(1)Py' to this compound, which is in satisfactory agreement with the mole ratio Cd(NO$_3$)$_2$: Py = 4 : 7. The recording of the sample DTA curve in a closed ampoule showed no thermal effects up to a temperature of

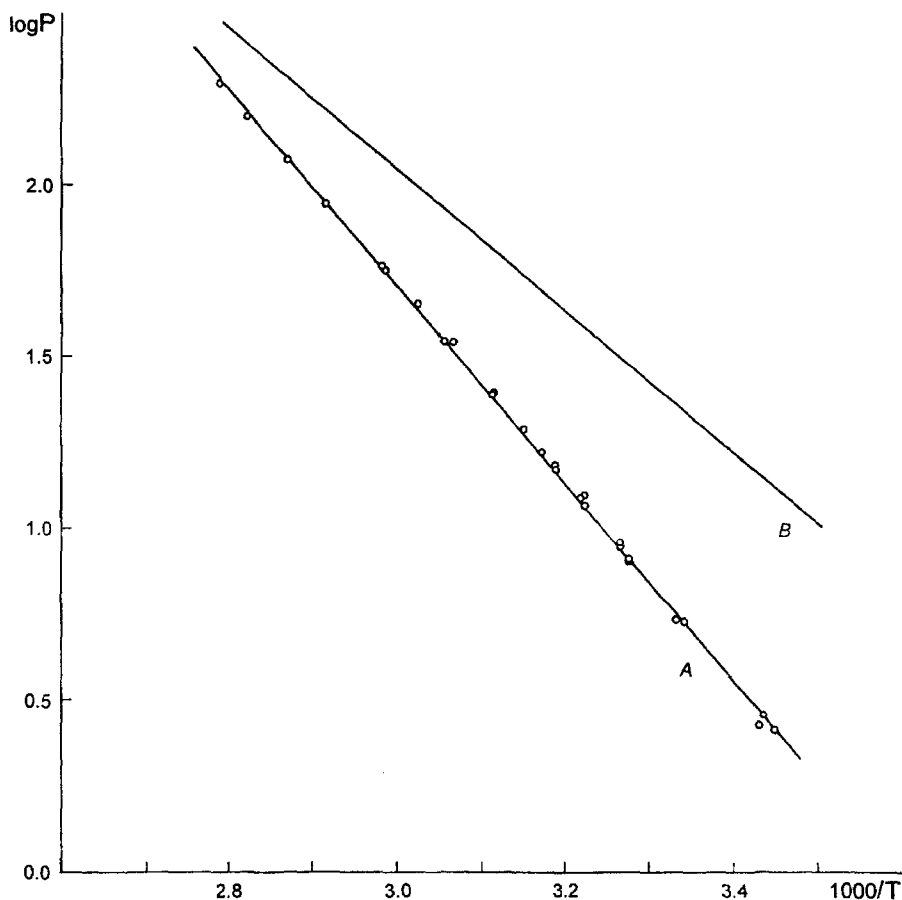*Figure 4.* Logarithm of pyridine vapour pressure versus the inverse temperature: A, over the clathrate [CdPy₄(NO₃)₂]·2Py; B, over liquid pyridine [25] (P, torr; T, K).

191 °C, at which it melted congruently. The same kind of DTA curve was obtained for a sample of the same composition obtained by the thermal decomposition of the complex $[CdPy_3(NO_3)_2]$ in a drying chamber. Thus, the resulting compound 'Cd(NO$_3$)$_2$·7/4Py' is really an individual phase. An attempt to obtain crystals suitable for the X-ray study was not successful. It seems likely that the authors of Ref. [20] dealt with the same compound, but they refer to it as $Cd_2Py_2(NO_3)_4$. Although their IR spectral studies of the compound did not yield reliable data on its structure, a polymeric one with bridgelike nitrate groups seems to be most likely. Note that the formation of dimeric, trimeric and polymeric structures with non-integer metal per pyridine base mole ratio is characteristic of cadmium complexes [26].

3.3. INTERRELATION BETWEEN THE STRUCTURES AND THE PROPERTIES OF THE COMPOUNDS

The clathrate $[CdPy_4(NO_3)_2] \cdot 2Py$ belongs to the group of clathrates of general formula $[MPy_4X_2] \cdot 2Py$ called 'orthorhombic clathrates', which at present includes about twenty compounds [1–3]. All of them are of molecular type and consist of *trans*-octahedral host-complex molecules and those of the guest-pyridine included in the channels situated along one of the crystallographic directions [3, 27]. The ordering and peculiar dipole order of guest pyridine species in the channels do not suggest their forward movement in this type of structure. Moreover, the study of these and other features of the packing of these clathrates suggests that if partial or complete removal of the guest-component occurs, the clathrate phase can hardly remain intact [27]. Indeed, the type of quasi-equilibrium TGA curves and especially the fact that changing the sample composition in the process of a strain experiment does not cause any changes in the temperature dependence of the pyridine vapour pressure over the clathrate are evidence for the absence of a solid clathrate solution area from the system. It should be emphasized that both of these techniques are very sensitive to the presence of solid solutions, which has been vividly shown by the example of similar systems [14]. Thus, the clathrate $[CdPy_4(NO_3)_2] \cdot 2Py$ is a compound of constant composition, and this is its fundamental difference from classic zeolite-like clathrates, e.g. β-phases formed by the $[Ni(MePy)_4(NCS)_2]$-host (MePy = 4-methylpyridine) [5].

The study of the system phase diagram also reveals that the removal of the guest causes decomposition not only of the clathrate phase but also of the host complex itself. As is clear from Figure 1, in this system the compound $[CdPy_4(NO_3)_2]$ has no stability area, i.e. the hypothetical phase of this composition is unstable, decomposing into the clathrate $[CdPy_4(NO_3)_2] \cdot 2Py$ and tripyridine complex $[CdPy_3(NO_3)_2]$. Thus, the molecules of *trans*-$[CdPy_4(NO_3)_2]$, where the cadmium cation is coordinated by four nitrogens of pyridine ligands and two oxygens of monodentate nitrate groups, can exist only in the clathrate phase due to contact stabilization when they are packed together with the guest molecules [7, 8]. The clathrate decomposition is accompanied by the splitting off of one of the pyridine ligands of the host molecule and results in the formation of the complex $[CdPy_3(NO_3)_2]$ where cadmium cation is coordinated by three pyridine nitrogens and four oxygens of two bidentate nitrate groups [23].

Alternatively, processes (1) and (2) can be thought of as proceeding in two qualitatively different stages: first, the removal of two moles of chemically unbound guest pyridine and second, the removal of one mole of ligand pyridine followed by a break of the coordination bond. However, these stages cannot be observed separately. Thus, in this system non-valent interactions make a contribution to the clathrate formation process comparable with that of chemical coordination bonds. Only under these conditions is the formation of unstable complex molecules in the clathrate phase possible, and this is the case with the system concerned.

Acknowledgements

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