Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Soldatov, Dmitriy V. , Ukraintseva, Elissa A. , Logvinenko, Vladimir A. , Dyadin, Yuri A. , Grachev, Eugeniy V. and Manakov, Andrey Yu.(2000) 'Thermodynamic Dissociation Constants for $[MPy_4(NO_3)_2]^*2Py$ Clathrates (M=Mn, Co, Ni, Cu)', Supramolecular Chemistry, 12: 2, 237 — 246

To link to this Article: DOI: 10.1080/10610270008027458

URL: http://dx.doi.org/10.1080/10610270008027458

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 237-246
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the Harwood Academic Publishers imprint,
part of the Gordon and Breach Publishing Group.
Printed in Malaysia

Thermodynamic Dissociation Constants for $[MPy_4(NO_3)_2]^*2Py$ Clathrates (M=Mn, Co, Ni, Cu)

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(In final form March 31, 2000)

Stoichiometry and thermodynamic parameters of the title clathrates dissociation have been studied with thermoanalytical and strain method techniques. The $[MPy_4(NO_3)_2]^*2Py$ (M = Mn, Co, Ni) clathrates dissociate with collapsing clathrate porous phase and destruction of the host complex to give the respective tripyridine complexes and gaseous pyridine. The $[CuPy_4(NO_3)_2]^*2Py$ dissociates with collapsing clathrate phase but giving the host $[CuPy_4(NO_3)_2]$ complex as individual phase, with the tripyridine complex forming in further course of decomposition. The comparison of the thermodynamic dissociation parameters for the $[MPy_4(NO_3)_2]^*2Py$ series with M = Mn, Co, Ni, Cu, Zn and Cd shows that the differences in the stability of the compounds do not correlate with structural parameters of the clathrates but depend on the nature of the metal cation in the host complex. Thermodynamic stability of these clathrate phases follows the general sequence of stabilty for complexes of the 3d transition metals known as Irwing-Williams sequence: Mn<Fe<Co<Ni<Cu>Zn. These results disclose the main issue of instability of the $[MPy_4(NO_3)_2]^*2Py$ clathrates as instability of the respective host complexes.

Keywords: Werner clathrates, thermodynamic constants, vapour pressure, pyridine, metal complex

INTRODUCTION

Structural investigations of hexapyridine addition compounds of many metal(II) salts revealed their supramolecular nature, with four pyridines coordinated to the metal and two included in the crystal framework, $[MPy_4X_2]^*2Py$.[2]Guest pyridine in $[CuPy_4(NO_3)_2]^*2Py$ was recently replaced with other components (benzene, tetrahydrofuran and chloroform)[3] that suggests its clathrate behavior. Therefore, on their structural and chemical properties, the compounds constitute new group of Werner clathrates.[4] In spite of many of the $[MPy_4X_2]^*2Py$ compounds have been studied X-ray structurally, little was made regarding the stoichiometry and stability region determinations for these compounds as well as the driving forces for their formation.

Structure of the compounds belonging to the clathrate series with nitrate host complexes $[MPy_4(NO_3)_2]^*2Py$ was determined earlier; the

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clathrates are isomorphous (M = M(II) = Mg,[5] Mn,[6]Co,[2] Ni,[2,7] Cu,[2,8] Zn,[2,9] Cd[2,10]). Our studies of phase equilibria in the pyridine – zinc nitrate[11-13] and pyridine – cadmium nitrate[13,14] systems uncovered formation conditions, thermal behavior and other important properties of respective clathrates. Only one clathrate compound forms in each system, the compound is of constant composition and the host complex does not appear as individual compound in all studied temperature-concentration conditions. The latter conclusion is of special interest as suggests possibility of obtaining molecules of unstable metal complexes inside clathrate phase, the phenomenon was referred to as contact stabilization phenomenon.[13,15] Further research on other members in the series assumed the above situation is general for the pyridine – metal(II) nitrate systems and only in Cu-one host complex was known, with the respective clathrate, $[CuPy_4(NO_3)_2]^*2Py$, showing surprisingly high thermal stability (Table I). The clathrate endures heating of up to 145°C melting incongruently to produce solid host complex at this temperature. The decomposition of its structural analogues occurs at lower temperatures by-passing the formation stage of host complexes undergoing further dissociation. The resulting tripyridine complexes, $[MPy_3(NO_3)_2]$, are isostructural to one another[6,17,18] as well as to $[CuPy_3(NO_3)_2]$[17] which forms during the $[CuPy_4(NO_3)_2]$ decomposition. From these data, we assumed that it is the strength of host complex coordination bonds that contributes mainly to overall stability of the resulting clathrate phases, rather than host-to-guest complementarity, which being a decisive factor for classical clathrates. Further elucidation of the problem required comparing thermodynamic dissociation parameters for this clathrate series. As such data had been available for the Zn-[12] and Cd-clathrates,[14] we determined decomposition stoichiometry and pyridine vapour pressure versus temperature over the title compounds.

TABLE I Melting points (°C) of some compounds forming in the pyridine – metal(II) nitrate systems

M	*$[MPy_3(NO_3)_2]$*	*$[MPy_4(NO_3)_2]$*	*$[MPy_4(NO_3)_2]^*2Py$*
Mn	**159**[6]	Unknown	**81**, dec.[6]
Co	**160**[16]	Unknown	**88**, dec. (this work)
Ni	**165**[16]	Unknown	**108** (this work)
Cu	**172** (this work)	**175** (this work)	**145**, dec. (this work)
Zn	**131**[11]	Unstable[11]	**62**, dec.[11]
Cd	**165**[14]	Unstable[14]	**106**, dec.[14]

EXPERIMENTAL SECTION

Preparations

Dinitratotetrapyridinemetal(II) – pyridine clathrates (1:2), $[MPy_4(NO_3)_2]^*2Py$ (M=Mn, Co, Ni)

Were prepared by recrystallizing, up to 4 times, the respective salts $M(NO_3)_2{}^*6H_2O$ (analytically pure grade) from pyridine, the procedure being similar to that for the Zn-[11]and Cd-analogues.[14] First crystallizations were performed using pyridine (analytically pure grade) containing 0.25% of water by mass. In last crystallizations, the pyridine was preheated dried by distillation over freshly calcined BaO and then kept over a 3 A zeolite ("reinst") for a week; the melting point was –43°C, the water content <0.02 mass%. Little ascorbic acid was added when preparing Mn-compound to prevent oxidation. The colourless (Mn), blue (Ni) and red (Co) crystalline clathrates were separated on a glass filter, air-dried for several minutes and stored in a desiccator over liquid pyridine and fused KOH. The *$[CuPy_4(NO_3)_2]^*2Py$* clathrate was obtained by saturating the $[CuPy_4(NO_3)_2]$ complex with pyridine vapours in a desiccator; the process was followed by changing colour from violet-lilac to blue and by weight rise of 2 moles of absorbed pyridine. Anal.(%):

Found: Mn, 8.41(5). $[MnPy_4(NO_3)_2]^*2Py$ requires: Mn, 8.41.

Found: Co, 8.90(8); Py, 72.9(6). $[CoPy_4(NO_3)_2]^*2Py$ requires: Co, 8.96; Py, 72.2.

Found: Ni, 8.99(6); Py, 73.1(6). $[NiPy_4(NO_3)_2]^*2Py$ requires: Ni, 8.93; Py, 72.2.

Found: Cu, 9.55(5); Py, 71.1(5). $[CuPy_4(NO_3)_2]^*2Py$ requires: Cu, 9.60; Py, 71.6.

Dinitratotetrapyridinecopper(II), $[CuPy_4(NO_3)_2]$

$Cu(NO_3)_2{}^*3H_2O$ (2.42 g, 0.01 mol; analytically pure grade) was dissolved in 20 ml acetone (of special purity grade) with the addition of concentrated nitric acid (4 or 5 drops) until the bright-blue solution turned out to transparent. A mixture of 5 ml acetone and 5 ml (0.062 mol) pyridine was then gradually added in there. After the reaction was complete the blue precipitate of $[CuPy_4(NO_3)_2]^*2Py$ was separated from the colourless solution on a glass filter, washed twice with acetone and exposed to air for delicate decomposition with occasional stirring. The final product was violet-lilac. The pyridine odour indicated that the decomposition was not yet complete whereas the appearance of seeds of the light-blue phase of tripyridine complex indicated that $[CuPy_4(NO_3)_2]$ had begun to decompose further and the drying was stopped immediately. The complex was stored in a tightly closed can. Yield on copper was 95% or more. Anal.(%):

Found: Cu, 12.55(5); Py, 61.9(4). $[CuPy_4(NO_3)_2]$ requires: Cu, 12.61; Py, 62.8.

Dinitratotripyridinecopper(II), $[CuPy_3(NO_3)_2]$

$[CuPy_4(NO_3)_2]$ (2.5 g) was suspended in 60 ml benzene; the mixture was next stirred for 10 min at 60–65°C, the suspended substance changing from violet-lilac to light-blue. The product was separated from hot supernatant solution on a glass filter, rinsed with 25 ml benzene and air-dried. Yield was 90% or more. The complex was stable. Anal.(%):

Found: Cu, 14.93(6); Py, 55.5(4). $[CuPy_3(NO_3)_2]$ requires: Cu, 14.96; Py, 55.9.

Dinitratotripyridinemanganese(II), $[MnPy_3(NO_3)_2]$

$[MnPy_4(NO_3)_2]^*2Py$ was decomposed under flow of dry air until 3 moles of pyridine loss. The product was dissolved in some excess of chloroform with addition of little pyridine, filtered and allowed to evaporate in dry atmosphere. Big crystals (colourless, with a touch of green) of the complex were separated, air-dried and were kept in a closed can. Anal.(%): Found: Mn, 13.09(5). $[MnPy_3(NO_3)_2]$ requires: Mn, 13.20.

The analyses for metal were performed by standard complexometric titration with EDTA solution; pyridine was determined potentiometrically by reverse titration with 0.4 M KOH solution (excess of 0.4M nitric acid was used for sample neutralization). At least three determinations were performed in each case.

Strain measurement

Pyridine vapour pressure over the compounds was measured by a static method using Pyrex membrane spoon-type null-manometers.[19] The membrane sensitivity varied from 0.03 to 0.1 torr (1 torr = 133.322 Pa) in different experimental series. The thermostatting and temperature measurement accuracy was 0.05 K. The volume of reaction vessel was about 50 ml. The membrane chamber was filled with the substances in a dry box and the chamber was sealed after evacuating. Other details of this technique and the scheme of used experimental set-up were given elsewhere.[20]

For the title clathrates, two or more experimental runs were performed in each case. The runs differed in sample quantity (typically in two times at sample mass of 1 to 3 g), with the reaction space volume being approximately the same. The observed coincidence (within experimental errors) of data obtained with the different ratios of the sample mass to the same reaction volume was assumed as evidence of monovariant character of the processes under study. The processes were well reversible, the equilibrium pressure established both in the direct and the backward course of reaction in a reasonable time (from one to several hours).

With the $[CuPy_4(NO_3)_2]$ complex one run over 337–392 K temperature range was performed (the pressure was <1 torr at lower temperatures). The complex dissociation was also reversible although the backward reaction was significantly slower.

Other methods

Melting points were measured with *DTA technique* using samples sealed into glass ampoules. Heating rate: 1 deg/min, accuracy of measuring phase transition temperatures: 0.9 deg or better.

The stoichiometry of dissociation processes was studied by *quasiequilibrium thermogravimetry*.[21] The mass loss curves were recorded on a MOM Q-1500-D derivatograph (Hungary) under quasi-isobaric, quasi-isothermal heating conditions at the rate of 0.3 mg/min, the mass of the samples was 150 mg. The set of standard holders employed provided the following range of pressures of the product gas: 0.01 (a plate crucible), 0.05 (an open one), 0.2 (a closed one), and 0.8 atm (a conic one).

Calculations

The experimental data on temperature dependence of pyridine vapour pressure over the compounds were approximated by linear equations $\log P = A - B/T$ (P, torr; T, K), with the coefficients A and B refined by least-squares technique. Data obtained in different runs for each compound were combined as no significant differences were found.

For packing coefficients, the volumes of the host and pyridine molecules were calculated using X-ray structural data for the clathrates (Mn,[6] Ni,[7]Cu,[8] Zn,[9] Cd[10]). As the structures of the Cu- and Zn-clathrates were determined at low temperatures, unit cell parameters measured at room temperature were applied for them from ref. 2.

RESULTS

From the quasiequilibrium thermogravimetry studies (Figure 1), three of the title clathrates, $[MPy_4(NO_3)_2]*2Py$ (M = Mn, Co, Ni), dissociate in one step to give tripyridine complexes:

$$[MPy_4(NO_3)_2]*2Py\ (solid) = [MPy_3(NO_3)_2]\ (solid) + 3Py\ (gas) \qquad (1)$$

This mode of dissociation holds in all applied range of the evolving pyridine pressures (with evident quantitative differences in decomposition temperatures). Therefore, the clathrate phase decomposition is accompanied by breakdown of the host complex $[MPy_4(NO_3)_2]$, the situation observed earlier for the analogous Zn-[11,13] and Cd-compounds.[13,14]

The Cu-clathrate demonstrates another mode. In the same range of experimental conditions its decomposition results in a host complex (eq. 2) which appears as a separate step on the mass loss curve (Figure 1) and only then decomposes further to give the tripyridine complex (eq. 3):

$$[CuPy_4(NO_3)_2]*2Py\ (solid) = [CuPy_4(NO_3)_2]\ (solid) + 2Py\ (gas) \qquad (2)$$

$$[CuPy_4(NO_3)_2]\ (solid) = [CuPy_3(NO_3)_2]\ (solid) + Py\ (gas) \qquad (3)$$

The data on the temperature dependence of the pyridine vapour pressure, taken from the strain experiments, are shown graphically in Figure 2. For comparison, analogous dependencies for pyridine vapour pressure over $[ZnPy_4(NO_3)_2]*2Py$,[12] $[CdPy_4(NO_3)_2]*2Py$,[14] and over neat pyridine[12] are presented as well. The data obtained with different ratios of the sample mass to the reaction volume do not differ within experimental errors for each clathrates what indicates monovariant type of the processes 1 and 2. This allows us to conclude that the four title clathrates are compounds of constant com-

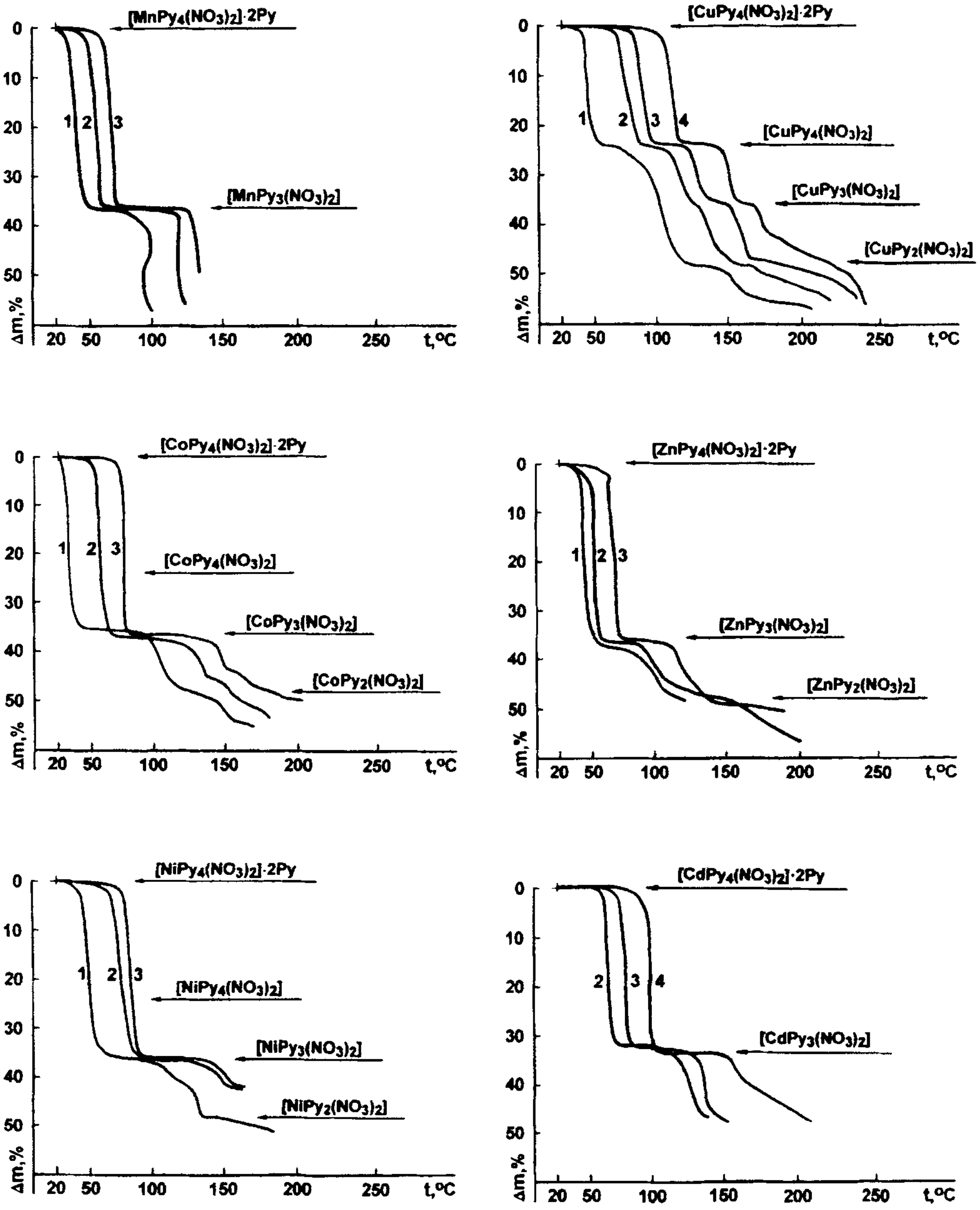

FIGURE 1 Mass loss curves for the $[MPy_4(NO_3)_2]\cdot 2Py$ clathrates (M=Mn, Co, Ni, Cu: this work; M=Zn, Cd: ref. 11,13,14). Sample holders: 1, plate; 2, open; 3, closed; 4, conic crucibles

position, with no significant area of solid solutions due to guest pyridine escape existing. The coefficients A and B of the equations $\log P = A - B/T$ approximating the data from the strain experiment are given in Table II, along with thermodynamic dissociation parameters calculated therefrom.

The dependencies for the Mn- and Co-clathrates (Figure 2) experience bend at 353 K (+80°C) (Mn) and 361 K (+88°C) (Co) which correspond

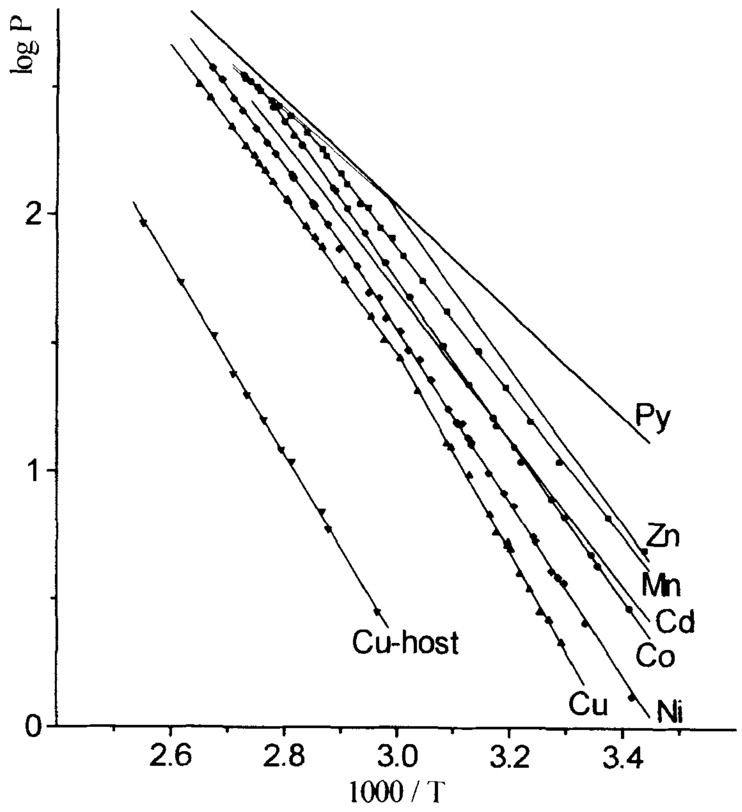

FIGURE 2 Temperature dependence of the pyridine vapour pressure over the $[MPy_4(NO_3)_2]\cdot 2Py$ clathrates (Mn, squares; Co, circles; Ni, diamonds; Cu, up triangles; Zn;[12] Cd[14]), over the $[CuPy_4(NO_3)_2]$ complex (Cu-host, down triangles), and over neat pyridine[12] (Py) in the logP – 1000/T coordinates (P, torr; T, K)

well to the incongruent melting points of the compounds[22] (cf. Table I). The dependencies for the Ni- and Cu-clathrates are also bent at approximately 344 K (71°C) and 333 K (60°C), respectively, suggesting polymorphous transformations of the clathrates.

DISCUSSION

Polymorphous transformations

From Table II, the thermodynamic parameters of polymorphous transformations observed for the Ni- and Cu-clathrates are as follows (the signs correspond to the transitions from low to high temperature modifications):

For $[NiPy_4(NO_3)_2]^*2Py$	For $[CuPy_4(NO_3)_2]^*2Py$
T=344 K (71°C)	T=333 K (60°C)
$\Delta H° = 22(2)$ kJ/mol	$\Delta H° = 35(2)$ kJ/mol
$\Delta S°_{298} = 65(5)$ J/(mol K)	$\Delta S°_{298} = 104(6)$ J/(mol K)
$\Delta G°_{298} = 3(2)$ kJ/mol	$\Delta G°_{298} = 4(1)$ kJ/mol

It is clearly seen that the transition into high-temperature modification occurs at the expense of significant entropy profit while the resulting change in free energy is not very big. This implies some rise in symmetry of the clathrate phase due to appearance of guest freedom degrees or slight changes in the host framework. Structural investigations of these phases at different temperatures would be very encouraged.

TABLE II Coefficients for the log P = A – B / T equations approximating pyridine vapour pressure temperature dependencies over the studied compounds (P,torr; T,K) and calculated thermodynamic parameters of the processes

$$1/3[MPy_4(NO_3)_2]\cdot 2Py\ (solid) = 1/3[MPy_3(NO_3)_2]\ (solid) + Py\ (gas) \tag{1a}$$

$$1/2[CuPy_4(NO_3)_2]\cdot 2Py\ (solid) = 1/2[CuPy_4(NO_3)_2]\ (solid) + Py\ (gas) \tag{2a}$$

$$[CuPy_4(NO_3)_2]\ (solid) = [CuPy_3(NO_3)_2]\ (solid) + Py\ (gas) \tag{3}$$

M	*Process*	*T-range*	*No. of exp. points*	*A*	*B/1000*	ΔH°_{av}[a] *kJ/mol*	ΔS°_{298}, *J/(mol K)*	ΔG°_{298}, *kJ/mol*
Mn	1a	292–353	18	10.31(4)	2.81(1)	53.8(3)	142.2(8)	11.4(5)
Co	1a	293–360	21	11.06(3)	3.106(9)	59.5(2)	156.6(6)	12.8(2)
Ni	la	293–347	29	11.68(7)	3.37(2)	64.6(4)	168(1)	14.4(6)
		347–374	11	10.56(4)	2.99(2)	57.2(3)	146.9(9)	13.4(4)
Cu	2a	304–333	15	13.2(2)	3.90(5)	74.6(9)	197(3)	15.9(5)
		333–378	17	10.43(4)	2.99(2)	57.2(3)	145(9)	14.1(4)
Cu	3	338–392	11	11.3(1)	3.66(4)	70.1(7)	162(2)	21.9(9)

a. Average value for studied temperature interval.

Of special interest is the transition in the Cu-clathrate phase. Without the change occurring higher 333 K the pyridine pressure over the clathrate would reach that over neat pyridine at ca. 372 K (99°C) making impossible its existence at higher temperatures. Meanwhile, the compound is stable (in close volume) up to 418 K (145°C). The mechanism of this polymorphous transformation may be analogous with that for the $[CdPy_4(NO_3)_2]$*2Py which was studied in detailes.[10]At 221 K (-52°C) the clathrate undergoes solid-phase change, with the host framework transforming from P (sp group *Pcca*) to C-lattice (*Ccca*). Notably, the Cu-clathrate crystallizes in primitive unit cell (*Pnna*)[8] while the rest clathrates from the series do in C-lattice (*Ccca*).[2,5,6,7,9,10]Our preliminary studies[23] revealed transformation of the $[CuPy_4(NO_3)_2]^*2Py$ clathrate into the *Ccca* space group at elevated temperatures. This may be the general tendency for the $[MPy_4X_2]^*2Py$ clathrates, with the realization of transition of this type and its temperature depending on nature of the metal M and ligand X. Clathrates with azide ligand in host complex, $[MPy_4(N_3)_2]^*2Py$ (M=Ni and Co), crystallize in *Pnna* space group at room temperature[24] while the majority of others do in *Ccca*, including those with cyanate.[25] If so, these compounds may be convenient models for studying the simplest solid-state reactions in clathrates of molecular metal complexes.

Clathrate stability in the $[MPy_4(NO_3)_2]^*2Py$ series: qualitative consideration

The results on equilibria during the title clathrates dissociation together with those for the analogous Zn-[11-13] and Cd-clathrates[13,14]allow the general tendencies in the compounds' behavior to be rationalized. In five cases of six the decomposition of the clathrate is accompanied not only with collapse of the clathrate phase but also with destruction of the host complex (eq. 1). (For the Zn-[11] and Cd-compounds[14], it was proved by the phase diagram determinations that the respective host complexes do not form at all as individual phases in the systems.) At the same time, X-ray structural investigations[6,7,9,10] give unequivocal evidence of existing the host molecules inside clathrates. Thus, being unable to create its own phase the molecules are stabilized by non-valent contact with guest species, the contact stabilization phenomenon[13,15]is observed here. The situation with

$[CuPy_4(NO_3)_2]^*2Py$ is qualitatively different. The clathrate dissociates with collapsing clathrate microporous phase but the host molecules keep themselves creating dense phase of the $[CuPy_4(NO_3)_2]$ composition. Two possible explanations of this difference may be done. First, this may be a matter of structural peculiarities of six-coordinated Cu-complexes. In the crystal structure of the $[CuPy_4(NO_3)_2]$[26] the Cu-N_{Py} distances are within 2.01–2.03 Å while the axial bonds are elongated as much as to 2.61 Å. Being admissible for copper, this type of coordination is hardly possible for other metals concerned. Second explanation may be in the highest strength of coordination bond of copper(II) compared to the other cations available in the complexes under consideration.[27]

The available data on Werner clathrates, both presented here and known before, give good illustration on different degrees of clathrate phase instability as well as possible sources of this instability. So-called β-phases of some Werner complexes with 4-alkylpyridine ligands, such as β-$[Ni(MePy)_4(NCS)_2]$, exemplify the situation when both host molecules and the very clathrate phase they build up are quite stable to exist for a long time even after complete guest removal.[28] The analogous Zn-complex can not be separated as individual phase while its molecules are found in clathrates of the complex.[29] Structural identity of β-$[Zn(MePy)_4(NCS)_2]^*MePy$ clathrate to its Ni-counterpart allows to conclude it is instability of the host molecule that is responsible for instability of the β-$[Zn(MePy)_4(NCS)_2]$ phase after guest removal. Then, the situation with studied in this work $[CuPy_4(NO_3)_2]$ is quite contrary: the complex molecules are able to exist out of clathrate creating its own phase while the clathrate phase can exist only at full occupancy of cavities with guest. Finally, the $[MPy_4(NO_3)_2]^*2Py$ clathrates of Mn-, Co-, Ni-, Zn-and Cd-hosts represent the extreme degree of instability: both complex molecules and the clathrate phase are unstable without guest component.

Clathrate stability in the $[MPy_4(NO_3)_2]^*2Py$ series: quantitative consideration

Further comparison of the clathrate stability in the $[MPy_4(NO_3)_2]^*2Py$ series will be done in terms of thermodynamic parameters for the clathrates' dissociation. This thermodynamic description may be done as a function of nature of metal cation forming the host complex. Such consideration seems to be quite strict due to the same stoichiometry of the dissociation processes (eq. 1) and structural identity of both clathrates and products of their dissociation (gaseous pyridine and isostructural tripyridine complexes). For the Cu-clathrate, the sum of the processes 2 and 3 may be used equivalent to 1.

Thermodynamic constants of the process 1 for the series are listed in Table III. Due to mentioned identity, differences in packing energy should not contribute significantly to the constants. It is the strength of the metal-pyridine bond rather than structural features that should have predominant influence on differences in listed thermodynamic constants. Indeed, thermodynamic stability of the clathrates in the series does not correlate with packing coefficients[30] (see Table III) or other structural parameters, the correlation usually found for clathrate compounds. The stability of these clathrate phases follows general stability sequence for complexes of first transition decade (so-called Irwing-Williams sequence[27]):

$$\mathrm{Mn} < \mathrm{Fe} < \mathrm{Co} < \mathrm{Ni} < \mathrm{Cu} > \mathrm{Zn}$$

This demonstrates how the host complex coordination bonds strengthening, the factor appears to be decisive here, results in progressive rise in the clathrate phase stability. Notably, the enthalpy contribution to free energy turns out to be dominant as the entropy part contributes in opposite way. This provides further evidence of predominant influence of metal-to-ligand coordination bond on change in stability in this clathrate series.

TABLE III The comparison of the pyridine – metal(II) nitrate systems: packing coefficients of the isomorphous clathrates $[MPy_4(NO_3)_2]\cdot 2Py$ (k_{pack}) and thermodynamic parameters for the process

$$[MPy_4(NO_3)_2]^*2Py\ (solid) = [MPy_3(NO_3)_2]\ (solid) + 3Py\ (gas) \quad (1)$$

M	k_{pack}	*T-range*	ΔH°_{av},^{a} *kJ/mol*	ΔS°_{298}, *J/(mol K)*	ΔG°_{298}, *kJ/mol*	*Ref.*
Mn	0.660(3)	292–353	161.4(8)	427(2)	34(1)	This work
Co		293–360	178.4(5)	470(2)	38.3(7)	This work
Ni	0.672(3)	293–347	194(1)	505(4)	43(2)	This work
		347–374	172(1)	441(3)	40(1)	
Cu	0.669(3)	304–333^b	219(3)	556(8)	54(2)	This work
		333–378^b	185(1)	451(4)	50(2)	
Zn	0.663(3)	300–335	175(2)	475(6)	33(3)	12
Cd	0.659(3)	290–360	165(1)	426(3)	38(1)	14

a. Average value for studied temperature interval.

b. Assuming the dissociation parameters for the $[CuPy_4(NO_3)_2]$ complex in this temperature interval hold unchangeable.

So far we determined the measure of instability of a molecule qualitatively, as inability to create its own phase. As one can find in Table III, now we quantitatively determine this measure of instability. In all systems, except one, host complex can not be separated as individual compound and therefore direct measurements on its properties are impossible. Nevertheless, the complex may be studied successfully as an integral part of a clathrate compound it forms.

CONCLUSION

Conventional approach considers the clathrate stability as a result of complementarity between host and guest molecules. Indeed, this approach is quite justified provided the participating molecules are stable enough to keep themselves in all processes under consideration. It is evident however that the overall clathrate stability is made up not only of intermolecular interactions but also of stability of the very molecules a clathrate consists of. Therefore, the latter factor may be decisive, and this is the case with the $[MPy_4(NO_3)_2]^*2Py$ clathrate series. Difference in stability of these clathrates is determined by difference in stability of the respective host molecules although the very molecules are observed only in clathrate phase destroying along with the phase upon guest removal.

Acknowledgements

This work was carried out within Federal Special Program "State Foundation for Integration of High Education and Fundamental Science in 1997–2000", 2nd Division, Subdivision No 1.4.4.3.6., Grant No 274.

References

1. Results of this work were presented at X-th International Symposium on Molecular Recognition and Inclusion, Warsaw, June 1998.
2. Soldatov, D.V.; Lipkowski, J; *J. Struct. Chem.* **1995**, *36*, 979, and references therein.
3. Soldatov, D.V.; Dyadin, Yu. A.; Lipkowski, J.; Ogienko, A.G.; *Mendeleev Comm.* **1997**, 11.
4. Lipkowski. J.; in *Comprehensive Supramolecular Chemistry*, Vol. 6, MacNicol, D.D., Toda F. and Bishop, R. (Eds.), Pergamon, Exeter, 1996, pp. 691–714.
5. Soldatov, D.V.; Ripmeester, J.A.; *Supramol. Chem.* **1998**, *9*, 175.
6. Soldatov, D.V.; Lipkowski, J; *J. Struct. Chem.* **1998**, *39*, 238.
7. Soldatov, D.V.; Lipkowski, J; Grachev, E.V.; *J. Struct. Chem.* **1995**, *36*, 830.
8. Beurskens, G.; Martens, C.F.; Nolte, R.J.M.; Beurskens, P.T.; Smits, J.M.M.; *J. Chem. Crystallogr.* **1995**, *25*, 425.
9. Losier, P.; Zaworotko, M.J.; *J. Chem. Crystallogr.* **1996**, *26*, 277.

10. Soldatov, D.V.; Kolesov, B.A.; Lipkowski, J; Dyadin, Yu. A.; *J. Struct. Chem.* **1997**, *38*, 819.
11. Soldatov, D.V.; Logvinenko, V.A.; Dyadin, Yu. A.; *Russ. J. Inorg. Chem.* **1995**, *40*, 309.
12. Ukraintseva, E.A.; Soldatov, D.V.; Dyadin, Yu. A.; *Zh. Neorg. Khim* **1997**, *42*, 283 (*Russ*). [*Chem. Abstr.* **1998**, *128*, 27428u].
13. Dyadin, Yu. A.; Soldatov, D.V.; Logvinenko, V.A.; Lipkowski, J.; *J. Coord. Chem.* **1996**, *37*, 63.
14. Soldatov, D.V.; Dyadin, Yu. A.; Ukraintseva, E.A.; Kolesov, B.A.; Logvinenko, V.A.; *J. Incl. Phenom.* **1996**, *26*, 269.
15. Dyadin, Yu. A.; Kislykh, N.V.; *Mendeleev Comm.* **1991**, 134.
16. Tomasik, P.; Ratajewicz, Z.; *Pyridine-Metal Complexes*, in: *The Chemistry of Heterocyclic Compounds*, Newkome, G.R. and Strekowski, L. (Eds.), John Wiley & Sons, Inc., New York, 1985, vol. 14, pt. 6, pp. 1118–1119, 1452–1453.
17. Cameron, A.F.; Taylor, D.W.; Nuttall, R.H.; *J. Chem. Soc., Dalton Trans.* **1972**, 1603.
18. Cameron, A.F.; Taylor, D.W.; Nuttall, R.H.; *J. Chem. Soc., Dalton Trans.* **1972**, 1608.
19. (a) Jackson, C.G.; *J. Chem. Soc.* **1911**, *99*, 1608.
    (b) Suvorov, A.V.; *Termodinamicheskaya khimiya parooobraznogo sostoyaniya. Tenzimetricheskiye issledovaniya geterogennykh ravnovesij (Thermodynamic chemistry of gaseous state. Strain studies of heterogeneous equilibria)*, Khimiya, Leningrad, 1970, pp. 46–51 (in Russ.).
20. Ukraintseva, E.A.; Dyadin, Yu. A.; Kislykh, N.V.; Logvinenko, V.A.; Soldatov, D.V.; *J. Incl. Phenom.* **1995**, *23*, 23.
21. Paulik, F.; Paulik, J.; *J. Therm. Anal.*, **1973**, *5*, 253.
22. After incongruent melting of the $[MnPy_4(NO_3)_2]^*2Py$ and $[CoPy_4(NO_3)_2]^*2Py$ clathrates the equilibrium is monovariant as well, involving three phases: solid $[MPy_3(NO_3)_2]$, liquor, and gaseous pyridine. The pyridine pressure in that case is also described by the $\log P = A - B/T$ equations with the following coefficients: for the Mn-system, A=7.51(8) and B/1000=1.82(3) (5 exp. points in the 353–366 K T-range); for the Co-system, A=7.98(8) and B/1000=1.99(3) (3 exp. points in the 360–367 K T-range).
23. Soldatov, D.V.; Lipkowski, J.; will be published.
24. Soldatov, D.V.; Lipkowski, J.; *J. Incl. Phenom.* **1998**, *30*, 99.
25. Soldatov, D.V.; Dyadin, Yu. A.; Lipkowski, J.; Suwińska, K.; *Mendeleev Comm.* **1997**, 100.
26. Soldatov, D.V.; Suwińska, K.; Lipkowski, J.; in: *5th International Summer School on Supramolecular Chemistry*, Program and Abstracts, Ustron (Poland), June 1996, p. P-65.
27. Irving, H.; Williams, R.J.P.; *J. Chem. Soc.* **1953**, 3192. It should be mentioned, that sometimes, as concerned to fifth and sixth coordination sites about copper, this general tendency may be broken.
28. (a) Andreetti, G.D.; Bocelli, G.; Sgarabotto, P.; *Cryst. Struct. Comm.* **1972**, *1*, 51.
    (b) Lipkowski, J.; Majchrzak, S.; *Rocz. Chem.* **1975**, *49*, 1655.
29. Lipkowski, J.; Soldatov, D.V.; Kislykh, N.V.; Pervukhina, N.V.; Dyadin, Yu. A.; *J. Incl. Phenom.* **1994**, *17*, 305.
30. Kitaigorodsky, A.I. *Molecular Crystals and Molecules*, Academic Press: New York, 1973, p. 18.