

CLATHRATE FORMATION IN THE $[M(4\text{-MePy})_2(\text{NCS})_2]$ -4-MePy SYSTEMS, WHERE
M = Co(II), Ni(II), Zn(II), Cd(II); 4-MePy = 4-METHYLPYRIDINE

Yu.A. Dyadin, N.V. Kislykh, G.N. Chekhova, N.V. Podberezskaya,
N.V. Pervukhina, V.A. Logvinenko, I.M. Oglezneva
Institute of Inorganic Chemistry, Academy of Sciences of the
USSR, Siberian Branch, Novosibirsk 630090,
U.S.S.R.

ABSTRACT. A number of complexes $[M(4\text{-MePy})_n(\text{NCS})_2]$, where M = Co(II), Ni(II), Zn(II), Cd(II); n = 2 or 4 have been synthesized and phase diagrams $[M(4\text{-MePy})_2(\text{NCS})_2]$ -4-MePy have been studied. The forming compounds have been obtained and described with the help of IR-spectroscopy and thermal analysis. The structure of a molecular type with variable section channels, filled by two types guest-molecules (by a water molecule in the narrow part of the channel and by two 4-methylpyridine molecules in the broad part of the channel, with a total ratio guest: host being 1:1) for $[\text{Cd}(4\text{-MePy})_4(\text{NCS})_2] \cdot 0.67(4\text{-MePy}) \cdot 0.33\text{H}_2\text{O}$ has been defined by X-ray method. This clathrate is isostructural (X-ray powder diffractogram) to the anhydrous compound $[\text{Cd}(4\text{-MePy})_4(\text{NCS})_2] \cdot 0.67(4\text{-MePy})$.

1. INTRODUCTION

In the present communication we discuss the results of the investigation of the phase diagrams of the systems $[\text{MB}_2\text{X}_2]$ -B (where M = Co(II), Ni(II), Zn(II), Cd(II); B = 4-methylpyridine; X = NCS⁻). This technique provides reliable data on the number of phases in the system, their compositions and areas of stability, the mode of their behaviour when the conditions of equilibrium change. When possible, the phases discovered have been isolated and studied by various methods (first of all by X-ray structure ones), providing information on the nature of the compounds obtained.

2. MATERIALS AND METHODS

4-methylpyridine, purified according to [1], contained less than 0.03% of water, melted at 3.5°C, boiled at 145.5°C (P = 1 atm). A changed technique [2] was employed for synthesizing the complexes involved, the complexes with composition $[\text{MB}_2\text{X}_2]$ being obtained for Cd(II) and Zn(II). To obtain $[\text{CdB}_4\text{X}_2]$ equivalent amount of KSCN was added to the 0.5 M aqueous solution $\text{Cd}(\text{NO}_3)_2$. 4-methylpyridine was added to the solution formed in drops, while the solution was mixed intensively. The complex obtained was filtered and washed by 5% 4-methylpyridine solution.

Clathrates were synthesized either by cooling the saturated solutions of the corresponding complexes in 4-methylpyridine or by saturation of the complexes by the guest through the gas phase in a closed vessel.

The metal content in the compounds was determined by complexometric titration with disodium EDTA solution [3]. Water was analyzed according to K.Fisher.

Phase equilibria were studied by the DTA method (the error was equal to $\pm 0.4^\circ\text{C}$). The samples studied were prepared of the $[\text{MB}_n\text{X}_2]$ ($n = 2$ or 4) complexes and 4-methylpyridine in ampoules, which were then sealed. Thermal effects, corresponding to the phase transformations, were measured repeatedly.

The liquidus curve was determined by the solubility method. The Cd-clathrate composition at different temperatures was determined by the analysis of the crystals, formed during the isothermal evaporation of the saturated solution after drying them by filter paper (at the same temperature). The most accurate data on the clathrates composition were obtained at room temperature by the saturation of the initial complexes by 4-methylpyridine through the gas phase.

IR-spectra in the area of $400\text{--}4000\text{ cm}^{-1}$ have been obtained by a UR-20 spectrometer. The samples were prepared as tablets with KBr and suspension in nujol.

Thermal dissociation of the compounds has been studied under quasi-equilibrium conditions (Q-derivatograph [4]). During the investigation of compounds (EGD, 10 mg sample) thermal dissociation kinetic curves of gas evolution were processed using computer programs [5].

The clathrate $[\text{CdB}_4\text{X}_2] \cdot 0.67\text{B} \cdot 0.33\text{H}_2\text{O}$ single crystals have been obtained by a slow recrystallization from the solution of $[\text{CdB}_4\text{X}_2]$ (saturated at 60°C) in 4-methylpyridine that has not been dried and contained up to 0.5% of water. During the diffractometer experiment the crystal was protected by silicate glue.

The intensities of all 5579 unique reflections were measured with automatic diffractometer "SYNTEX P2_I", using graphite-monochromatized MoK_α radiation (the $\theta\text{--}2\theta$ scan technique, V_{\min} of scan speed was 5 deg/min , no correction was made for absorption, $\mu_{\text{MoK}_\alpha} = 8.0\text{ cm}^{-1}$). A total $3612 > 3\sigma_I$ unique reflections were employed in calculation. The structure was determined by the application of heavy-atom method to Patterson and Fourier summations. All computations were carried out using the YANX crystallographic complexes of programs [6]. The refinement of the coordinates of the atoms was carried out using of full-matrix least-square procedures to $R = 0.077$.

3. RESULTS

3.1. The System $[\text{CdB}_2\text{X}_2]\text{--B}$ Phase Diagram

The data on the phase diagram are shown in Tables I and II, a general picture is given in Figure 1. Two compounds form in the system; $[\text{CdB}_4\text{X}_2] \cdot 0.67\text{B}$ with incongruent melting at 139.2°C and $[\text{CdB}_4\text{X}_2]$, that disproportionates according to reaction (6) at 134.0°C .

The clathrate has a constant composition in the temperature range

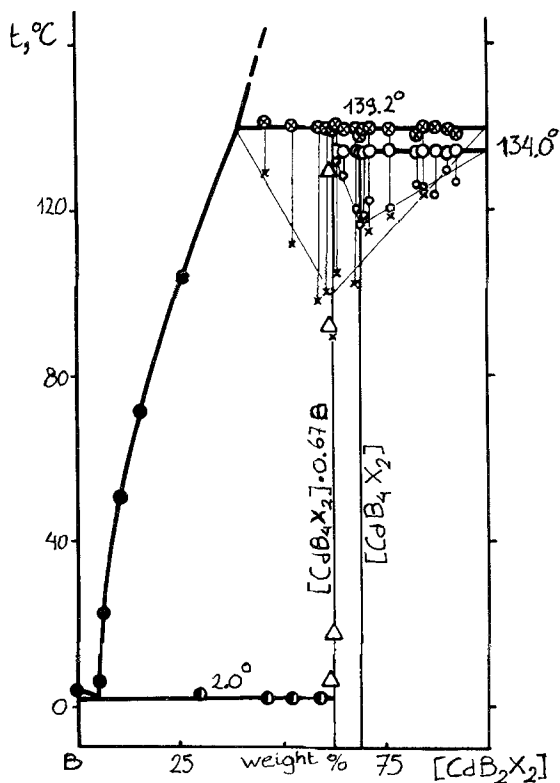


Figure 1. Binary system $[\text{CdB}_2\text{X}_2]$ -B phase diagram.

TABLE I. The liquidus curve of the system $[\text{CdB}_2\text{X}_2]$ -B.

$t, ^\circ\text{C}$	6.0	23.0	50.7	50.7	71.0	104.0
weight% $[\text{CdB}_2\text{X}_2]$	5.41	6.55	10.67	10.63	15.08	25.59

TABLE II. Solid clathrate phase composition at different temperatures.

$t, ^\circ\text{C}$	7.0	18.0**	91.5	129.0
mean weight% Cd	16.66		16.74	16.81
mean weight% $[\text{CdB}_2\text{X}_2]$	61.47	62.37±0.13	61.78±0.68	62.02±1.95*

* confidence range for 95% probability

** at 18±3°C (room temperature) the clathrate composition is determined during its synthesis through the gas phase.

studied (7 - 129°C) within the error of determination (Table II). The $[\text{CdB}_2\text{X}_2]$ complex decomposes irreversibly at 234.5°C.

3.2. IR-Spectroscopy Data

The initial 4-methylpyridine spectrum has been interpreted according to [7]. The absorption bands of both 4-methylpyridine and the NCS groups are present in the spectra of the complexes, the $\nu(\text{CN})$ intensive bands in the 2065-2105 cm^{-1} interval are indicative of the coordination of the NCS group with all the metals through nitrogen [8]. Noticeable changes are observed in the spectra of complexes and clathrates in comparison with the spectrum of 4-methylpyridine (Fig. 2).

The intensive band 487 cm^{-1} in the 4-methylpyridine spectrum according to [9] is due to the C-C and C-H rotatory vibrations. As for hexacoordinated complexes it is shifted in the direction of higher frequencies: 498 cm^{-1} for Ni(II), 497 cm^{-1} for Co(II), 491 cm^{-1} for Cd(II). In the tetraordinated complexes spectra this band splits into two components, besides the intensive band, a band of average intensity appears in the range of lower frequencies: 480 and 493 cm^{-1} for Zn(II), 468 and 491 cm^{-1} for Cd(II). The 516 cm^{-1} band observed in the 4-methylpyridine spectrum in the spectra of all the complexes is also shifted in the direction of the higher frequency (Fig. 2).

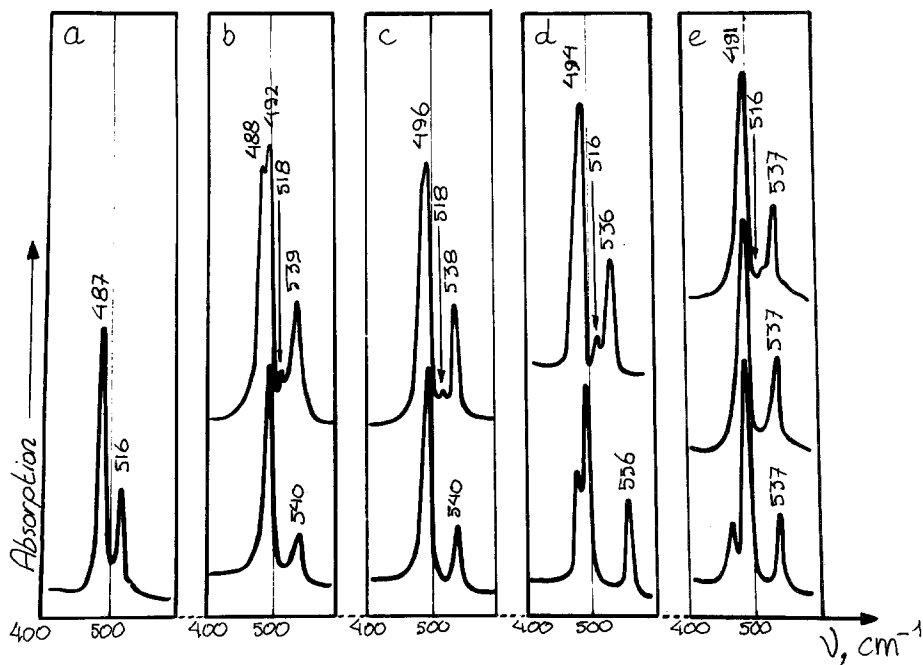
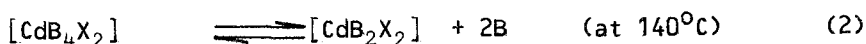


Figure 2. IR-Spectra in 400-600 cm^{-1} range:
 a) 4-methylpyridine; b) 1. $\alpha\text{-}[\text{NiB}_4\text{X}_2]$, 2. $[\text{NiB}_4\text{X}_2]\cdot\text{B}$;
 c) 1. $[\text{CoB}_4\text{X}_2]$, 2. $[\text{CoB}_4\text{X}_2]\cdot\text{B}$; d) 1. $[\text{ZnB}_2\text{X}_2]$, 2. $[\text{ZnB}_4\text{X}_2]\cdot\text{B}$;
 e) 1. $[\text{CdB}_2\text{X}_2]$, 2. $[\text{CdB}_4\text{X}_2]$, 3. $[\text{CdB}_4\text{X}_2]\cdot 0.67\text{B}$.

3.3. The Thermogravimetric Analysis Data

When the thermal dissociation of the compounds in the selfgenerated atmosphere of 4-methylpyridine (the labyrinth sample holder, $P = 1$ atm, $DTG = 0.2$ mg/min) was being studied, their decomposition temperatures were measured:



Since under these conditions the decomposition temperatures are the temperatures, corresponding to one and the same equilibrium constant, equal to one ($P = 1$ atm), they can be considered to be units of measurement of thermodynamic stability of the compounds of this set.

The study of the thermal dissociation kinetics of the compounds showed in all cases the decomposition process to be described by the shrinking sphere equation ($n = 2/3$). The kinetic parameters (in flowing helium) were the following:

for reaction (1) - $t_{\text{in}} = 51^\circ\text{C}$, $E = 111$ kJ, $\lg A = 13.4$;

for reaction (2) - $t_{\text{in}} = 34^\circ\text{C}$, $E = 103$ kJ, $\lg A = 12.6$;

for the reaction



$t_{\text{in}} = 120^\circ\text{C}$, $E = 150$ kJ, $\lg A = 15.2$.

The mean square error $\sigma_E \approx \pm 4\%$, $\sigma_{\lg A} \approx \pm 4\%$.

3.4. Description of the $[\text{CdB}_4\text{X}_2] \cdot 0.67\text{B} \cdot 0.33\text{H}_2\text{O}$ Clathrate Structure

The crystals are triclinic with unit cell dimensions $a = 17.726$ (4), $b = 16.942$ (5), $c = 11.262$ (4) Å, $\alpha = 76.83$ (3), $\beta = 115.06$ (2), $\gamma = 122.50$ (2)°, $V = 2515.3$ (1.3) Å³, $P1$, $d_m = 1.311$ (4), $d_x = 1.32$ g/cm³, $Z = 3$. As a whole, the structure is of a molecular type, it is formed by the $[\text{CdB}_4\text{X}_2]$ host molecules and the guest molecules of two types: those of 4-methylpyridine and a water molecule (the ratio guests sum: host = 1:1). Three crystallographically independent Cd atoms have an octahedral environment, consisting of 4N(B)-rings and 2N isothiocyanate groups: (Cd 1-N)_{mean} 2.38 (3), (Cd 2-N)_{mean} 2.38 (3), (Cd 3-N)_{mean} 2.40 (3) Å.

The host molecules are pseudocentrosymmetric, the maximum deviation of the atom coordinates being 0.03 from the ideal values. Cd-octahedra are arranged in the apices, in the middle of the α edge and in the centre of the θc face of the unit cell. A channel of anisodiametric type stretching along c is formed in the centre of the unit cell (the molecule packing and the cross-section of the channel are shown in Fig. 3). The maximum channel section ($z \approx 0$, $r \approx 3.6$ Å) is occupied by two 4-methylpyridine molecules, the minimum one ($z \approx 0.5$, $r \approx 2.0$ Å) - by the H₂O mole-

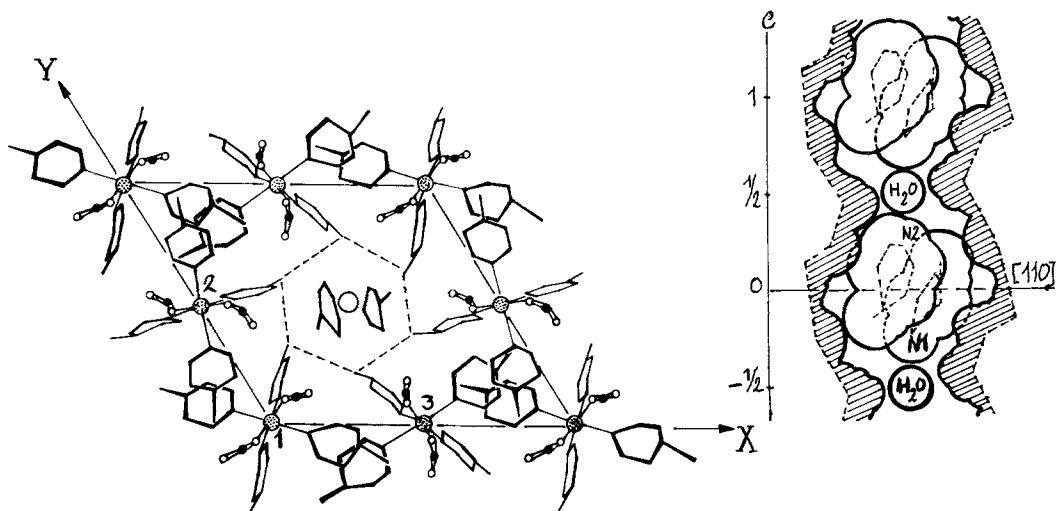


Figure 3. Clathrate $[\text{CdB}_4\text{X}_2] \cdot 0.67\text{B} \cdot 0.33\text{H}_2\text{O}$ structure: a) structure projection on the plane (001); b) guest-molecules arrangement in clathrate channel; 1,2,3 - designations of the Cd-atoms.

cule, the guests are linked by Van der Waals distances $\text{N} \dots \text{O}$ 2.89 and 2.98 Å. The mean of the bond lengths and the valency angles in (B)-rings are 1.36, 1.41 for N-C and C-C; 121, 122 and 118° for $\angle\text{CNC}$, $\angle\text{NCC}$, $\angle\text{CCC}$ respectively. The valency angles in the thiocyanate groups (162-177, mean 174°) are indicative of the nonlinearity of some of them. The calculation of the torsion angles φ and α shows that "++--" (1) and "+---" (2) conformations occur in three independent host molecules according to Lipkowsky's terms [10].

The X-ray powder method showed that the compound, containing almost no water (less than 0.08 weight%), is isostructural with the clathrate compound $[\text{CdB}_4\text{X}_2] \cdot 0.67\text{B} \cdot 0.33\text{H}_2\text{O}$ described above, the latter melting incongruently at $136.4 \pm 0.5^\circ\text{C}$.

3.5. The Study of $[\text{Ni}, \text{CoB}_4\text{X}_2]\text{-B}$ and $[\text{ZnB}_2\text{X}_2]\text{-B}$ Systems

Some data on the phases, forming in these systems, have been obtained (Table III). The difference in the pressures of the evolving gas for the DTA method (a sealed ampoule) and TG-analysis (a labyrinth sample holder) accounts for the difference in the decomposition temperatures for $[\text{NiB}_4\text{X}_2]$ and $[\text{NiB}_4\text{X}_2] \cdot \text{B}$. X-Ray powder diffractograms showed that Ni- and Co-clathrates are isostructural and differ from Zn and Cd-clathrates, differing from each other.

TABLE III. Some properties of the phases studied.

Compound	t ₁ , °C	t ₂ , °C	d, g/cm ³
α-[NiB ₄ X ₂]	208.6	165	-
[NiB ₄ X ₂]·B	153.8	130	1.257±0.001 ^{a)}
[CoB ₄ X ₂]	188.4		-
[CoB ₄ X ₂]·B	88.6		1.247±0.003
[ZnB ₂ X ₂]	191.1 ^{b)}		-
[ZnB ₄ X ₂]	69.3		-
[ZnB ₄ X ₂]·B	63.7		1.255±0.004
[CdB ₂ X ₂]	234.5 ^{c)}		-
[CdB ₄ X ₂]	134.0	140	-
[CdB ₄ X ₂]·0.67B	139.2	140	1.31 calc.
[CdB ₄ X ₂]·0.67B·0.33H ₂ O	136.4		1.311±0.004

t₁ - temperature of decomposition in sealed ampoules,

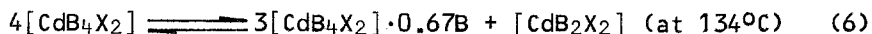
t₂ - temperature of decomposition in labyrinth sample holder,

a) density calculated from X-ray data [11] is equal to 1.244 g/cm³,

b) congruent melting, c) decomposes irreversibly.

4. DISCUSSION

In the [CdB₂X₂]-B system we managed to find only one clathrate compound, a phase with a constant composition. The peculiarity of this system is that the temperature of the host complex [CdB₄X₂] decomposition into a clathrate and the [CdB₂X₂] complex (134°C) is lower than the clathrate melting temperature (139.2°C). Since the [CdB₄X₂] complex decomposition goes according to reaction (6) without weight loss, as it should be expected the complex compound thermogram (Q-derivatograph) shows the effect of the subsequent clathrate decomposition (reaction 1, 140°C):



The comparison of the clathrate compound composition with the structural data shows, that compound is stable when the cavities (the broadenings in the channel) are fully occupied by 4-methylpyridine molecules, each cavity being occupied by two molecules. The shape of the channels in this clathrate compound structure in general outline resembles the [NiB₄X₂] β-phase channels [12] (alternation of broadenings and narrowings). A water molecule is situated in the narrow part of the channel, which in this case causes a general mole ratio guest: host = 1:1, the solid phase containing more water in comparison with the equilibrium liquid phase. Therefore, obtaining an anhydrous clathrate requires carefully dried products. As has already been mentioned, the removal of water from the clathrate does not result in the change of its structure, from which it follows, that the narrow part of the channel can remain hollow. Moreover, the inclusion of water not only does not cause an additional stabilization, but even slightly destabilizes the structure.

The IR-spectroscopy data (Fig. 2), which agree with the structural data, are indicative of the presence of 4-methylpyridine of two types in clathrate compounds: bonded (a ligand) and "free" (a guest), which can most obviously be demonstrated by the $[\text{NiB}_4\text{X}_2] \cdot \text{B}$ clathrate spectrum.

It is common knowledge, that even one and the same NiB_4X_2 complex can give different clathrate frameworks [10] depending on the guest (β , γ and, perhaps, one more structure [13]). According to our data Cd(II) and Zn(II) complexes produce clathrate structures having no analogues. The further widening of the set of metals can be expected to increase the number of clathrate structure types, as it is in the case of Hoffman-Iwamoto's compounds [14]. The ability of one and the same host to form clathrate structures of several types is not characteristic of only the complexes concerned. This is known also to be characteristic of other host-components (e.g., TOT [15] and, especially, water [16]).

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