Pyridine vapour pressure over $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Co, Ni) clathrates

Elissa A. Ukraintseva, Dmitriy V. Soldatov, Vladimir A. Logvinenko and Yuri A. Dyadin*

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 3832 35 5960; e-mail: clat@che.nsk.su

Pyridine vapour formation from the title clathrates is accompanied by the destruction of both the clathrate phase and the host complex: $^1/_3[MPy_4(NO_3)_2]\cdot 2Py$(solid) = $^1/_3[MPy_3(NO_3)_2]$(solid) + Py(gas); the standard thermodynamic parameters of these processes are $\Delta H^0 = 59.5(2)$ and 64.6(4) kJ mol^{-1}, $\Delta S^0_{298} = 156.6(6)$ and 168(1) J mol^{-1} K^{-1}, $\Delta G^0_{298} = 12.8(2)$ and 14.4(6) kJ mol^{-1}, for the Co- and Ni-clathrate, respectively.

The systems pyridine base (A) – metal(II) salt (MX_2) also form, along with purely coordination compounds, clathrate compounds of the general formula $[MA_4X_2]\cdot y$A. In these structures, chemically nonbound molecules of A (the 'guest') occupy the molecular framework cavities of the $[MA_4X_2]$ complex (the 'host') and can be replaced by other organic components.[1] It was only very recently[2] that a number of compounds formed in systems with A = unsubstituted pyridine were established to have a clathrate nature, although the compounds themselves were already known earlier. Almost all of them are described by the general formula $[MPy_4X_2]\cdot 2Py$ *i.e.* their limiting guest to host molar ratio (*y*) is equal to 2. Still more recently, many of them have been studied X-ray structurally: $[MPy_4Br_2]\cdot 2Py$ (M = Mg,[3] Co, Ni,[2] Cu[2,4,5]), $[MPy_4I_2]\cdot 2Py$ (M = Co,[2] Cu[6]), $[NiPy_4(NCS)_2]\cdot 2Py$,[7] $[NiPy_4(HCOO)_2]\cdot 2Py$,[2] $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Co,[2] Ni,[2,8] Cu,[2,9] Zn, Cd[2,10]). However, these structural data do not allow any conclusions to be made regarding the stability and stability regions of these compounds as well as the driving forces for their formation. Up to now, there have been hardly any studies enabling conclusions about the stoichiometry of these compounds to be drawn: whether they are solid solutions (*y* varies over a certain interval) or have a constant composition (*y* = 2 and the phase collapses as the guest is removed). This communication presents the results of our study of the $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Co, Ni) clathrates using strain and quasiequilibrium thermogravimetry techniques capable of giving answers to the above questions.

The $[MPy_4(NO_3)_2]\cdot 2Py$ (M = Co, Ni) clathrates were obtained by recrystallizing, 4 times, the respective salts $M(NO_3)_2\cdot 6H_2O$ (analytically pure grade) from pyridine.[2] The first two crystallizations were performed using pyridine (analytically pure grade) containing 0.25% of water by mass. In the last two crystallizations, the pyridine was preheated by distillation over freshly calcined BaO and then kept over a 3 Å zeolite ('reinst') for a week; the melting point is –43 °C, the water content < 0.02 mass%. The 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 analysis for metal was performed by EDTA titration with Murexide as indicator and the analysis for pyridine, by back acid–base titration. Calc. for $[CoPy_4(NO_3)_2]\cdot 2Py$ (%): Co, 8.96, Py, 72.2. Found: Co, 8.90(8); Py, 72.9(6). Calc. for $[NiPy_4(NO_3)_2]\cdot 2Py$ (%): Ni, 8.93; Py, 72.2. Found: Ni, 8.99(6); Py, 73.1(6). The Co-clathrate melts incongruently at 87–88 °C. The Ni-clathrate melts congruently at 107–108 °C.

The thermal decomposition of the clathrates was studied by quasiequilibrium thermogravimetry.[11] The mass loss curves were recorded at the rate of 0.3 mg min^{-1}, the mass of the samples was 150 mg. The set of standard crucibles employed made possible the following range of pressures of the product gas: 0.01 (a plate crucible), 0.05 (an open one), and 0.20 atm (a closed one).

In the strain experiment, the vapour pressure was measured by a static method using Pyrex membrane spoon-type null-manometers (for a detailed description of the experimental set-up see ref. 12). The membrane sensitivity was 0.03–0.1 torr.[†] The thermostatting and temperature measurement accuracy was 0.05 K. The membrane chamber was filled with the substances under study in a chamber with P_2O_5.

For the Co-compound, three experimental runs over the temperature range from 293 to 360 K and at various sample quantity (or primary composition) to reaction space volume (*ca.* 55 ml) ratios have been performed. The first run of the experiments was performed with 2 g of the clathrate; in the second run, 3.55 g of the clathrate was used. The third run was a continuation of the second run. After the second run was complete, 5 mg of pyridine (0.6% of the guest pyridine mass in the initial sample) was removed (frozen through the gas phase into a special side vessel which was then sealed off) from the system. For the Ni-compound, two runs of experiments were performed in the temperature interval from 293 to 374 K using 1.5 g of the clathrate in the first run and 2.3 g in the second.

The processes under study turned out to be completely reversible. The equilibrium pressure established during 1–3 h both in the direct and the back course of the processes.

The experimental data obtained are summarized in Figure 1 in the log *P*–1000/*T* coordinates together with the analogous dependence for pure pyridine.[13] The numeric data on the pyridine vapour pressure are approximated by the equations

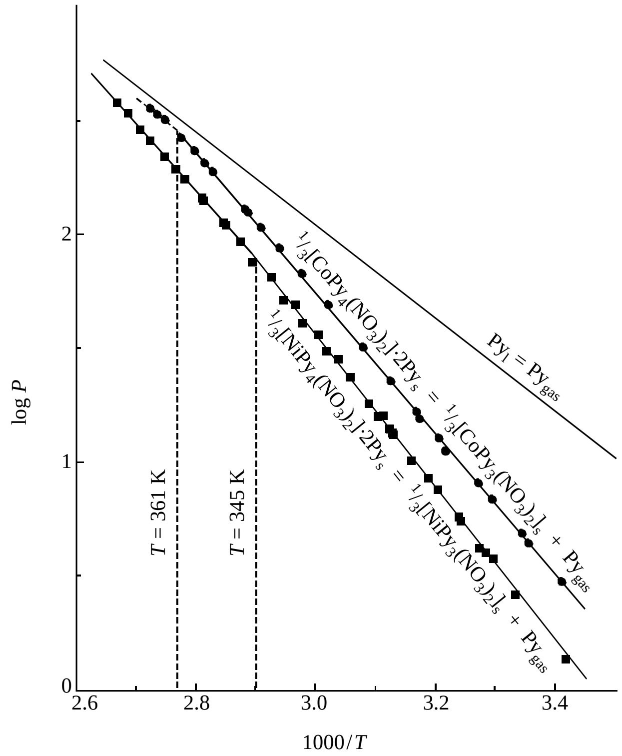

Figure 1 Temperature dependence of the pyridine vapour pressure over the title clathrates (our experimental data) and over liquid pyridine[13] in the log *P*–1000/*T* coordinates (*P*/torr; *T*/K).

[†] Further in the text the pressure is given in torr; 1 torr = 133.322 Pa.

Table 1 Coefficients for the log $P = A - B/T$ equations approximating pyridine vapour pressure temperature dependences over the title clathrates (P/torr; T/K) and calculated thermodynamic parameters of the process $^{1}/_{3}$[MPy$_4$(NO$_3$)$_2$]·2Py(solid) = $^{1}/_{3}$[MPy$_3$(NO$_3$)$_2$](solid) + Py(gas).

M	Temperature range	A	B/1000	ΔH^0/kJ mol^{-1}	ΔS^0_{298}/J mol^{-1} K^{-1}	ΔG^0_{298}/kJ mol^{-1}
Co	293–360	11.06(3)	3.106(9)	59.5(2)	156.6(6)	12.8(2)
Ni	293–345	11.68(7)	3.37(2)	64.6(4)	168(1)	14.4(6)
Ni	345–374	10.56(4)	2.99(2)	57.2(3)	147.9(9)	13.4(4)

log $P = A - B/T$ with the coefficients cited in Table 1. The temperature dependence of the pyridine vapour pressure over the [CoPy$_4$(NO$_3$)$_2$]·2Py clathrate at 361 K (88 °C) experiences a bend due to incongruent melting of the clathrate. The analogous dependence for the [NiPy$_4$(NO$_3$)$_2$]·2Py clathrate also has a feature in the form of a bend at approximately 345 K (72 °C). The most probable explanation for this bend is a polymorphous transition assosiated either with the liberation of the degrees of freedom of the guest pyridine or with a change in the nature of bonding in the host molecule itself, as observed earlier for the analogous [CdPy$_4$(NO$_3$)$_2$]·2Py at 221 K (–52 °C).[14]

The main qualitative result of the strain experiment is that the pyridine vapour pressure over each of the clathrates is independent of the ratio of the initial sample weight to the reaction space volume, *i.e.* is independent of the solid sample composition. This indicates the absence, in these systems, of regions of solid clathrate solutions or, in other words, the clathrate dissociation process is monovariant in each case and involves three phases. The quasiequilibrium thermogravimetric data (Figure 2)[‡] showed these phases to be the solid clathrate [MPy$_4$(NO$_3$)$_2$]·2Py, the solid tripyridine complex [MPy$_3$(NO$_3$)$_2$] and gaseous pyridine and over the whole range of temperatures studied the process is described by the equation:

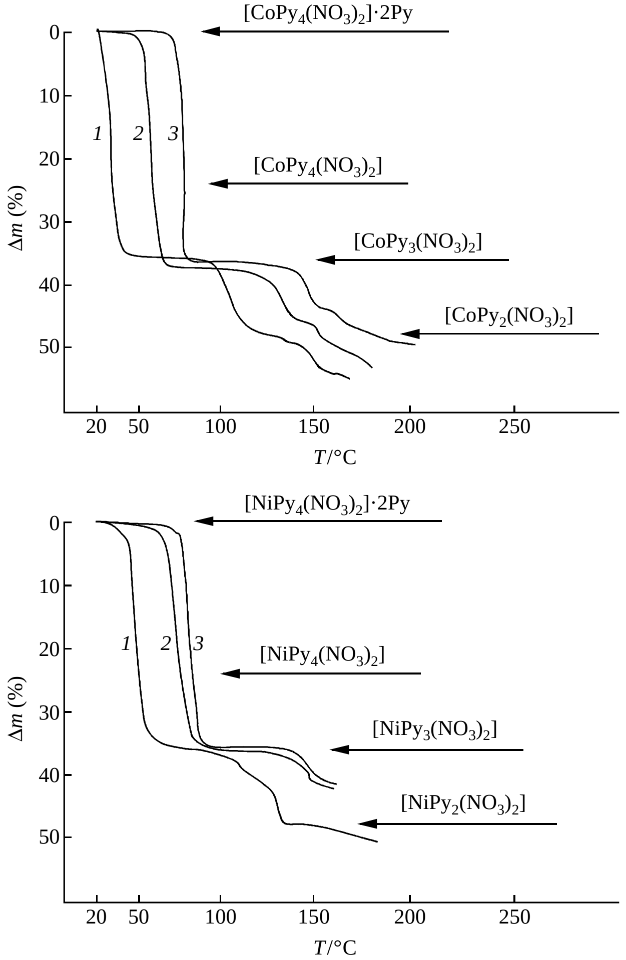

Figure 2 Mass loss curves for the title clathrates. Heating program: quasiisobaric–quasiisothermal; q = 0.3 mg min^{-1}; sample holders: *1*, plate; *2*, open; *3*, closed crucibles.

$$^{1}/_{3}[\mathrm{MPy_4(NO_3)_2}]\cdot 2\mathrm{Py(solid)} = {}^{1}/_{3}[\mathrm{MPy_3(NO_3)_2}](\mathrm{solid}) + \mathrm{Py(gas)} \quad (1)$$

Thus, the two clathrates studied are compounds of a constant composition, *i.e.* the clathrate phase is only stable if all of the cavities are filled dissociate as the guest is removed. Moreover, with the removal of the guest there simultaneously takes place destruction of the host complex from which one of the pyridine ligands splits off. The standard enthalpies, entropies and Gibbs energies of the process (1) derived from the strain experiment in the respective temperature intervals are given in Table 1.

Process (1) for the Co- and Ni-compounds is completely analogous since the clathrates are isostructural[2] and the resulting products are also very similar, according to the magnetic, conductometric and infra-red vibrational data.[15] Therefore, the substantial differences in decomposition temperature for the clathrates in the respective crucibles (Figure 2), in the equilibrium vapour pressure over the clathrates (Figure 1), and in their melting point suggest a second important conclusion. These differences appear to be due not to the packing factors, which are practically the same for these systems, but rather they are associated with the strength of the host complex, in our case with the differences in the strength of the metal–pyridine ligand coordination bond. In other words, it is the stability limit of the host complex itself that primarily determines the stability limit of each of the clathrates.

The results obtained indicate the occurrence in these systems of contact stabilization, a phenomenon where favourable non-valent interactions in the clathrate phase stabilize the complex host molecules.[16] In some cases this results in a greater thermal stability of the clathrate as compared with the individual phase of the host complex and in other cases leads to a situation where the host complex does not exist at all as an individual phase and its molecules form and actually exist in the clathrate phase.[10,16,17] So far in the literature there have been no reports of the isolation of individual [CoPy$_4$(NO$_3$)$_2$] and [NiPy$_4$(NO$_3$)$_2$] complexes so that clathrate formation is probably the only way to obtain these complexes within a solid phase composition.

The work was in part supported by the UNI-028-95 project within the ‘Universities of Russia’ program. We wish to thank V. A. Titov for valuable remarks when interpreting the experimental data.

References

1 J. Lipkowski, in *Inclusion Compounds*, Academic Press, London, 1984, vol. 1, p. 59.
2 D. V. Soldatov and J. Lipkowski, *Zh. Strukt. Khim.*, 1995, **36**, 1070 (*Russ. J. Struct. Chem.*, 1995, **36**, 979).
3 A. F. Waters and A. H. White, *Aust. J. Chem.*, 1996, **49**, 35.
4 M. Selkti, C.-C. Ling and A. Navaza, *J. Incl. Phenom.*, 1994, **17**, 127.
5 D. V. Soldatov, *J. Incl. Phenom.*, 1995, **20**, 191.
6 P. B. Durand and E. M. Holt, *Acta Crystallogr.*, 1995, **C51**, 850.
7 D. V. Soldatov and J. Lipkowski, *Zh. Strukt. Khim.*, 1995, **36**, 1074 (*Russ. J. Struct. Chem.*, 1995, **36**, 983).
8 D. V. Soldatov, J. Lipkowski and E. V. Grachov, *Zh. Strukt. Khim.*, 1995, **36**, 912 (*Russ. J. Struct. Chem.*, 1995, **36**, 830).

[‡] As illustrated in Figure 2, the clathrate dissociation takes place directly into tripyridine complexes, by-passing the formation stage of the host-complexes [MPy$_4$(NO$_3$)$_2$]. Furthermore, the tripyridine complexes decompose in the plate crucible into dipyridine complexes whereas irreversible transformations assosiated with nitrate dissociation occur in the uncovered and closed crucibles.

9 G. Beurskens, C. F. Martens, R. J. M. Nolte, P. T. Beurskens and J. M. M. Smilts, *J. Chem. Crystallogr.*, 1995, **25**, 425.
10 Yu. A. Dyadin, D. V. Soldatov, V. A. Logvinenko and J. Lipkowski, *J. Coord. Chem.*, 1996, **37**, 63.
11 F. Paulik and J. Paulik, *J. Therm. Anal.*, 1973, **5**, 253.
12 E. A. Ukraintseva, Yu. A. Dyadin, N. V. Kislykh, V. A. Logvinenko and D. V. Soldatov, *J. Incl. Phenom.*, 1995, **23**, 23.
13 E. A. Ukraintseva, D. V. Soldatov and Yu. A. Dyadin, *Zh. Neorg. Khim.*, 1997, **42**, 283 (in Russian).
14 B. A. Kolesov, D. V. Soldatov and Yu. A. Dyadin, *Mendeleev Commun.*, 1996, 249.
15 R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 383.
16 Yu. A. Dyadin and N. V. Kislykh, *Mendeleev Commun.*, 1991, 134.
17 J. Lipkowski, D. V. Soldatov, N. V. Kislykh, N. V. Pervukhina and Yu. A. Dyadin, *J. Incl. Phenom.*, 1994, **17**, 305.

Received: Moscow, 4th October 1996
Cambridge, 20th March 1997; Com. 6/06938J