Thermodynamic dissociation constants for the $[Cu(py)_4(NO_3)_2]\cdot 2py$ clathrate and $[Cu(py)_4(NO_3)_2]$ complex

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A comparison of the determined thermodynamic dissociation parameters for $[Cu(py)_4(NO_3)_2]\cdot 2py$ with those for analogous Mn, Co, Ni and Zn clathrates indicates the stability of the host molecules as the main contribution to the stability of the resulting clathrates.

Supramolecular compounds $[M(py)_4(NO_3)_2]\cdot 2py$ (M = Mg, Mn, Co, Ni, Cu, Zn or Cd) form in the pyridine (py)–metal(II) nitrate systems.[1–7] There are two types of pyridine molecules in the compounds: ligated to the metal atom (ligand pyridine) and located inside crystal framework cavities (guest pyridine). Our studies of the Cu system revealed a surprisingly high stability of the $[Cu(py)_4(NO_3)_2]\cdot 2py$ clathrate as well as the $[Cu(py)_4(NO_3)_2]$ host complex formed in the system (Table 1).[†] The clathrate endures heating of up to 145 °C melting incongruently to produce the solid host complex at this temperature. The decomposition of its structural analogues formed in the Mn, Co, Ni, Zn and Cd systems occurs at lower temperatures without the stage of formation of the host complexes which undergo further dissociation. The resulting tris(pyridine) complexes, $[M(py)_3(NO_3)_2]$, are isomorphous to one another[2,12,13] as well as to $[Cu(py)_3(NO_3)_2]$[12] which forms during the $[Cu(py)_4(NO_3)_2]$ decomposition. From these data, we assumed that it is the strength of host complex coordination bonds that mainly contributes to the overall stability of the resulting clathrate phases, rather than the host-to-guest complementarity, which is a decisive factor for classical clathrates.[14] To provide support for this assumption, it was necessary to compare thermodynamic dissociation parameters for this clathrate series. As such data had been available for all the clathrates of transition metal complex hosts except the Cu system,[9,11,15,16] we determined the pyridine vapour pressure over the title compounds as a function of temperature.

Synthesis and analysis of the compounds were described earlier.[17] The stoichiometry of dissociation was studied with the quasi-equilibrium thermogravimetry method.[‡,18] The numerical data on the equilibrium pyridine vapour pressure over the title compounds as a function of temperature were measured using a strain technique.[§]

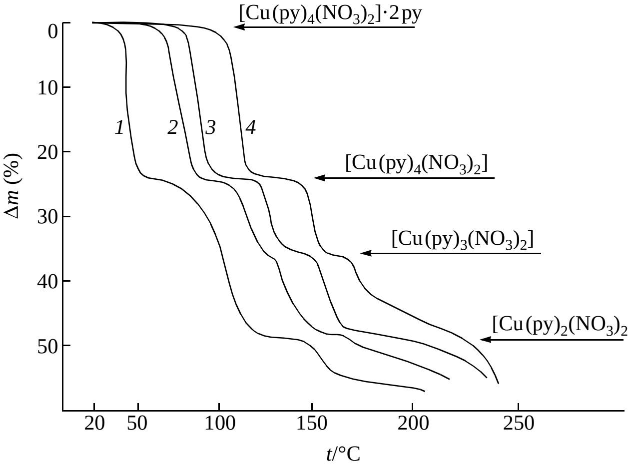

Figure 1 Mass loss curves for $[Cu(py)_4(NO_3)_2]\cdot 2py$. Sample, 150 mg; atmosphere, air; heating, quasi-isobaric–quasi-isothermal; $q = 0.3$ mg min^{-1}; sample holders: (*1*) plate, (*2*) open, (*3*) closed and (*4*) conic crucibles.

Table 1 Melting points (°C) of some compounds in the pyridine–metal(II) nitrate systems.

M	$[M(py)_3(NO_3)_2]$	$[M(py)_4(NO_3)_2]$	$[M(py)_4(NO_3)_2]\cdot 2py$	Reference
Mn	159	unknown	81 (decomp.)	2
Co	160	unknown	88 (decomp.)	8 and 9
Ni	165	unknown	108	8 and 9
Cu	172	175	145 (decomp.)	this work
Zn	131	unstable	62 (decomp.)	10
Cd	165	unstable	106 (decomp.)	11

The mass loss curves for $[Cu(py)_4(NO_3)_2]\cdot 2py$ are shown in Figure 1. The clathrate dissociates with formation of the host complex:

$$[Cu(py)_4(NO_3)_2]\cdot 2py\ (solid) = [Cu(py)_4(NO_3)_2]\ (solid) + 2py\ (gas) \quad (1)$$

The complex dissociates further:

$$[Cu(py)_4(NO_3)_2]\ (solid) = [Cu(py)_3(NO_3)_2]\ (solid) + py\ (gas) \quad (2)$$

The data on the vapour pressure are shown in Figure 2. The temperature dependence of the pyridine vapour pressure during the clathrate dissociation exhibits a bend at approximately 333 K.[¶] The numerical data on the pyridine vapour pressure over the title compounds are approximated by the equations $\log P = A - B/T$. The coefficients and the calculated thermodynamic dissociation parameters are summirised in Table 2.

The parameters for the total transformation of the clathrate into the tris(pyridine) complex calculated from these data are given in Table 3 along with corresponding parameters for other

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[†] Melting points given in text and Table 1 were measured by DTA using samples sealed in glass ampoules. Heating rate: 1 K min^{-1}. Accuracy of phase transition temperatures 0.9 K or better. Note that under other conditions the compounds decompose at lower temperatures with the loss of pyridine (Figure 1).

[‡] MOM Q-1500-D derivatograph (Hungary). The mass loss curves were recorded at a rate of 0.3 mg min^{-1}, the mass of the samples was 150 mg. The set of standard holders provided the following pressures of the product gas: 0.01 (a plate crucible), 0.05 (an open crucible), 0.2 (a closed crucible) and 0.8 atm (a conic crucible).

[§] The vapour pressure was measured by a static method using a Pyrex spoon-type membrane as a null manometer.[19] The membrane sensitivity varied from 0.05 to 0.1 Torr in different experimental series. The accuracy of thermostatting and temperature measurements was 0.05 K. The volume of the reaction vessel was *ca.* 50 ml.

The membrane chamber was filled with substances in a dry box and sealed after evacuating. For $[Cu(py)_4(NO_3)_2]\cdot 2py$, two experimental runs over the temperature range 304–378 K were performed. Clathrate portions of 143 and 719 mg were used in the first and second runs, respectively, with the same reaction vessel volume. No significant difference between the data obtained in these two runs was observed. The clathrate dissociation is completely reversible; the equilibrium pressure established well both in the forward and backward directions. For $[Cu(py)_4(NO_3)_2]$, one run over the range 337–392 K was performed (the pressure was < 1 Torr at lower temperatures). The complex dissociation is also reversible although the backward reaction is significantly slower.

[¶] The bend corresponds to a polymorphous transformation of the clathrate. Possibly, it is analogous to the transformation of $[Cd(py)_4(NO_3)_2]\cdot 2py$ at 221 K.[7]

Table 2 Coefficients of the log $P = A - B/T$ equations and calculated thermodynamic parameters of reactions (1) and (2).

Reaction	Number of experimental points	T range/K	A	B/1000	ΔH°_{av} / kJ mol^{-1}	ΔS°_{av} / J mol^{-1} K^{-1}	ΔG°_{298} / kJ mol^{-1}
(1)	15	304–333	13.2(2)	3.90(5)	149(2)	394(6)	31.8(9)
(1)	17	333–378	10.43(4)	2.99(2)	114.4(6)	289(2)	28.2(8)
(2)	11	338–392	11.3(1)	3.66(4)	70.1(7)	162(2)	21.9(9)

clathrates of the $[M(py)_4(NO_3)_2]\cdot 2py$ series. Due to the isomorphism of both clathrates and tris(pyridine) complexes, the differences in packing energies are insignificant, and it is the strength of the metal–pyridine bond that should have a predominant influence on differences in listed thermodynamic constants for the following process:

$$[M(py)_4(NO_3)_2]\cdot 2py\ (\text{solid}) = [M(py)_3(NO_3)_2]\ (\text{solid}) + 3py\ (\text{gas}) \qquad (3)$$

For the Cu compound, reaction (3) is a sum of (1) and (2), while in other systems the intermediate host complex $[M(py)_4(NO_3)_2]$ does not form an individual phase.

The dependence of the clathrate dissociation parameters on the nature of metal in the host complex (Table 3) confirms this hypothesis. The thermodynamic stability of the clathrates in the series does not correlate with packing coefficients[††,20] or other structural parameters; a correlation was usually found for clathrate compounds.[14] At the same time, the order of stability of these clathrate phases follows the general stability sequence for complexes (Irwing–Williams sequence[21]) Mn < Fe < Co < < Ni < Cu > Zn.

This demonstrates how the strengthening of the coordination bonds of the host complex results in a progressive rise in the clathrate phase stability. Note that in the majority of systems the host complex is insufficiently stable to form its own, non-clathrate, phase. This phenomenon, when the molecules unable to create a phase can be stabilised by non-covalent contact with molecules of another type, was referred to as contact stabilisation of molecules.[22] So far we have determined the measure of instability of a molecule as the inability to have its own phase. Here, we quantitatively determine this measure of instability (Table 3). Only in the Cu system, the host molecule can form a stable host phase. This qualitative change manifests itself as a steep quantitative rise in the thermal and thermodynamic stability of the clathrate formed by the complex.

The conventional approach considers the stability of clathrates as a result of the complementarity between host and guest molecules. Indeed, this approach is quite justified provided the participating molecules are stable enough to prevent dissociation during all processes under consideration. It is evident, however, that the overall stability of clathrates depends not only on intermolecular interactions but also on the stability of the component molecules. Therefore, the latter factor may be decisive, and this is the case with the clathrate series under consideration.

Table 3 The comparison of the pyridine–metal(II) nitrate systems. Packing coefficients (k_{pack}) of the isomorphous clathrates $[M(py)_4(NO_3)_2]\cdot 2py$ and thermodynamic parameters of reaction (3).

M	k_{pack}	T range/K	ΔH°_{av} / kJ mol^{-1}	ΔS°_{av} / J mol^{-1} K^{-1}	ΔG°_{298} / kJ mol^{-1}	Reference
Mn	0.660(3)	292–352	160.8(9)	424(3)	34(2)	15
Co		293–360	178.4(5)	470(2)	38.3(7)	9
Ni	0.672(3)	293–345	194(1)	505(4)	43(2)	9
Cu	0.669(3)	304–333[a]	219(3)	556(8)	54(2)	this work
		333–378[a]	185(1)	451(4)	50(2)	this work
Zn	0.663(3)	300–335	175(2)	475(6)	33(3)	16
Cd	0.659(3)	290–360	165(1)	426(3)	38(1)	11

[a] For the Cu system, reaction (3) is the sum of (1) and (2), which were studied in different temperature ranges (Table 2); here, we assume that the dissociation parameters for the $[Cu(py)_4(NO_3)_2]$ complex in the indicated temperature interval are the same as in the temperature range studied.

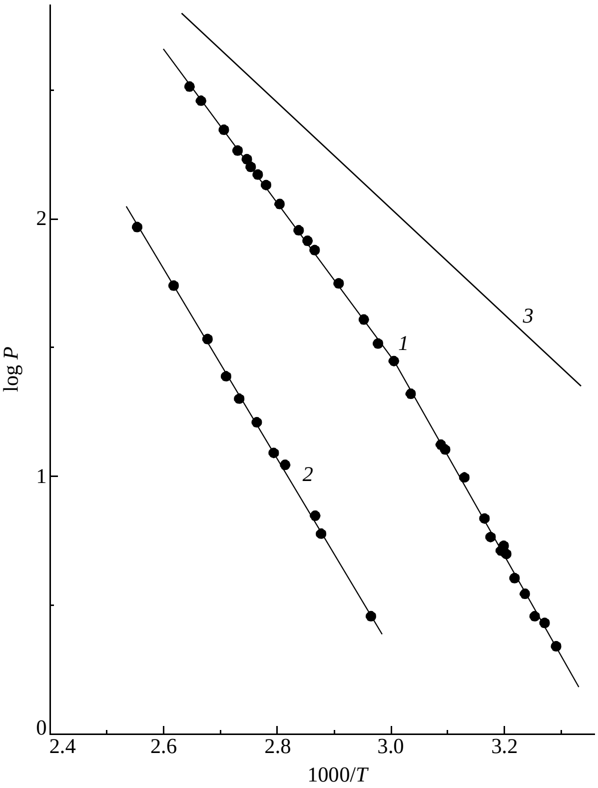

Figure 2 Temperature dependence of the pyridine vapour pressure over (*1*) $[Cu(py)_4(NO_3)_2]\cdot 2py$ and (*2*) $[Cu(py)_4(NO_3)_2]$ (experimental data) and (*3*) over liquid pyridine[16] on the log P – 1000/T coordinates (P/Torr, T/K).

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[††] The volumes of the host and pyridine molecules were calculated using X-ray structural data for the clathrates (Mn,[2] Ni,[4] Cu,[5] Zn[6] and Cd[7]). As the structures of the Cu and Zn clathrates were determined at low temperatures, the unit cell parameters measured at room temperature were taken from ref. 3.

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