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Structure and supramolecular nature of the compounds $[MPy_4(NCO)_2]\cdot 2Py$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd)[†]

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The seven title compounds form a series of isostructural clathrates of orthorhombic type.

X-Ray crystallography and spectroscopic studies of a row of $MX_2\cdot 6Py$[†] compounds have revealed their supramolecular nature.[1] The compounds consist of two types of molecules and should be formulated as $[MPy_4X_2]\cdot 2Py$. In the complex unit, coordinated to the central atom are two X anions in the *trans*-position and four pyridine ligands. The remaining two pyridine species are included in the cavities of the molecular framework of the complex. The fact that the non-bonded pyridine can be replaced by other components suggests a clathrate nature for the compounds of this row.[‡]

Structurally, most of the $[MPy_4X_2]\cdot 2Py$ clathrates studied belong to the orthorhombic type (space groups *Ccca* or *Pnna*). At the same time, they are rather varied in the qualitative composition of the host complex: M = M^{II} = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd; X = X^- = Br, I, HCOO, NO_2, NO_3. When the complex is axially elongated (due to elongation of the M–X bond or the X ligand itself) a tetragonal-type structure forms. This type of structure has been found for the $[CuPy_4(NO_3)_2]\cdot 2C_6H_6$[2] (*I422*) and the $[NiPy_4(NCS)_2]\cdot 2Py$[3] ($I4_1/acd$) clathrates.

The compounds of general composition $M(NCO)_2\cdot 6Py$ studied in this work were known previously (except for the Zn-compound) but were not characterized structurally. An examination of the electronic and IR spectra for the compounds of Ni[4] and Fe[5] indicated the presence of two types of pyridine in each compound, coordinated and free. These data, as well as a comparison with the above $[MPy_4X_2]\cdot 2Py$ clathrates, suggest the title compounds could have an analogous structure, *i.e.* are $[MPy_4(NCO)_2]\cdot 2Py$ clathrates. The present work was aimed at providing evidence in support of this hypothesis. The structural assignment of the possible clathrates was also of great interest, more so since the geometry of the NCO^- group is intermediate between the X ligands being responsible for the orthorhombic and tetragonal structures.

The compounds were obtained by a modification of known methods.[5–7] In the first stage, tetra- or dipyridine complexes were synthesized and the final stage included their recrystallization from pure pyridine.[§]

(I) $M(NO_3)_2\cdot xH_2O\ +\ 2KOCN\ +\ yPy\ \longrightarrow$
$[MPy_y(NCO)_2]\downarrow\ +\ 2KNO_3\ +\ xH_2O$
M = Mn, Co, Ni: $x = 6$, $y = 4$; water as solvent
M = Fe: Mohr's salt $[FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O]$ instead of nitrate, $y = 4$; water
M = Cu: $x = 3$, $y = 2$; water–ethanol (1:1)
M = Cd: $x = 4$, $y = 2$; water–ethanol (1:1)
M = Zn: $x = 6$, $y = 2$; water

(II) $[MPy_y(NCO)_2]\ +\ (6-y)Py\ \longrightarrow\ [MPy_4(NCO)_2]\cdot 2Py$

The compounds were obtained as air- and heat-sensitive substances of stoichiometric composition.[¶,††] Unit cell parameters and space group of the clathrates were determined on CAD-4 (Ni-compound) and KM-4 (the rest) single crystal diffractometers.[‡‡] For the $[NiPy_4(NCO)_2]\cdot 2Py$ clathrate, the structure was determined fully.[§§]

The main conclusion of the work is that the title compounds are indeed clathrates of the general formula $[MPy_4(NCO)_2]\cdot 2Py$.

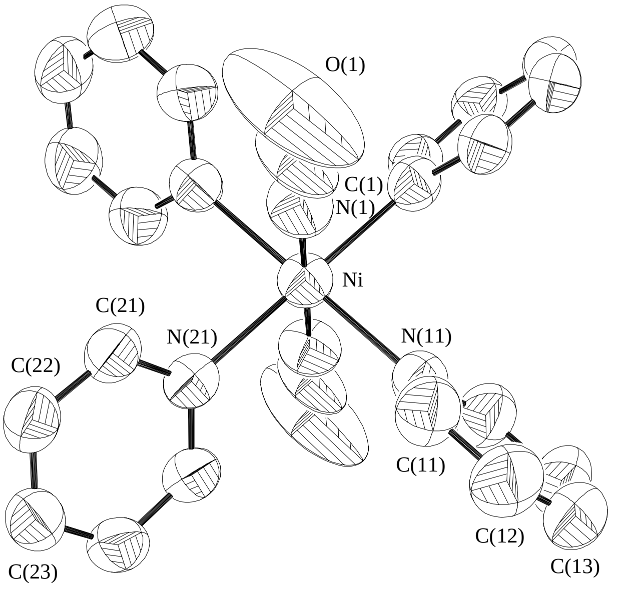

Figure 1 ORTEP-projection of the complex molecule found in the $[NiPy_4(NCO)_2]\cdot 2Py$ clathrate. H atoms are omitted. The main interatomic distances/Å: Ni–N(1) 2.054(5), Ni–N(11) 2.176(4), Ni–N(21) 2.147(4), N1–C(1) 1.108(7), C(1)–O(1) 1.190(8). The angles between the coordination bonds are right angles, the isocyanate group is linear.

[†] M = metal(II), X = univalent acido group, Py = pyridine.

[‡] Replacement of the guest pyridine with benzene, tetrahydrofuran and chloroform has been performed for the $[CuPy_4(NO_3)_2]\cdot 2Py$ clathrate.[2]

[§] *Synthesis of* $[NiPy_4(NCO)_2]\cdot 2Py$: Solutions of $Ni(NO_3)_2\cdot 6H_2O$ (5.82 g, 0.02 mol; analytically pure grade) in 15 ml water and KOCN (3.24 g, 0.04 mol; pure) in 15 ml water were poured together and 6 ml dimethylformamide was then added. To the stirred green-yellow solution was added, dropwise, during 0.5 h, a mixture of pyridine (10 ml, > 0.12 mol; analytically pure grade) and 10 ml water. The blue crystalline precipitate of the $[NiPy_4(NCO)_2]$ complex was separated on a glass filter, washed twice with 10 ml of a 5% aqueous solution of pyridine and once with 10 ml water and then air-dried. The complex obtained (8.1 g, 0.018 mol) was recrystallized from 80 ml hot (90 °C) pyridine (containing a maximum 0.2% water). The crystalline clathrate was separated and dried on a glass filter until the first signs of decomposition appeared and then allowed to stay in a desiccator over pyridine for three days where it was then stored. Yield 10.8 g (90% on Ni).

[¶] The colour and temperatures of decomposition (incongruent melting in a closed volume) of the $[MPy_4(NCO)_2]\cdot 2Py$ clathrates obtained: M = Mn, white, 88–89 °C; Fe, yellow, 94–95 °C; Co, dark-red, 103–104 °C; Ni, blue, 118–119 °C; Cu, bright-blue, 62–63 °C; Zn, white, 15–17 °C; Cd, white, 85–86 °C.

[††] Analysis for metal was performed by titration: Mn, Co, Ni, Cu, Zn, Cd with EDTA; Fe, with potassium permanganate. Results {M: Found, Calc. for $[MPy_4(NCO)_2]\cdot 2Py$ (%)}: Mn: 8.92(3), 8.95; Fe: 9.16(4), 9.09; Co: 9.60(5), 9.54; Ni: 9.45(4), 9.51; Cu: 10.15(3), 10.21; Zn: 10.3(1), 10.5; Cd: 16.71(5), 16.75. Given in parentheses are standard deviations for three or more determinations.

Table 1 X-Ray diffraction data[a] for $[MPy_4(NCO)_2]\cdot 2Py$ clathrates studied and their comparison with parameters for the known $[MPy_4X_2]\cdot 2Py$ clathrates.

	M	Space group	a/Å	b/Å	c/Å	V/Å^3	$d_{calc.}{}^b$/g cm^{-3}	
	Mn	*Ccca*	12.525(4)	15.340(6)	16.792(3)	3226(2)	1.26	
	Fe	*Ccca*	12.456(2)	15.195(3)	16.856(3)	3190(1)	1.28	
	Co	*Ccca*	12.491(2)	15.075(2)	16.779(2)	3159(1)	1.30	
	Ni	*Ccca*	12.59(1)	15.03(1)	16.75(1)	3168(5)	1.30	
	Cu	*Ccca*	12.107(2)	15.034(2)	17.270(2)	3143(1)	1.32	
	Zn[c]	?	12.07(1)[c]	14.86(5)[c]	17.08(2)[c]	3064(11)[c]	1.35[c]	
	Cd	*Ccca*	12.482(5)	15.511(6)	16.822(8)	3257(2)	1.37	
X		Literature data						Ref.
ONO	Ni	*Ccca*	12.144(6)	14.94(1)	16.86(1)	3058(3)	1.36	8
NO_3	Ni	*Ccca*	12.148(5)	15.019(4)	16.96(1)	3095(3)	1.41	9
Br	Mg	*Ccca*	11.575(2)	14.999(4)	17.292(2)	3002(1)	1.46	10
Br	Cu	*Ccca*	12.033(8)	14.764(3)	16.768(5)	2978(2)	1.56	11, 12

[a]Given in parentheses are standard deviations. [b]Assuming $Z = 4$. [c]At –123 °C; the unit cell is rectangular within experimental error 0.3°.

As shown in Table 1, they crystallize in the space group *Ccca*; in the symmetry and unit cell parameters they are analogous to known orthorhombic clathrates with other X: $[NiPy_4(ONO)_2]\cdot 2Py$,[8] $[NiPy_4(NO_3)_2]\cdot 2Py$,[9] $[MgPy_4Br_2]\cdot 2Py$[10] and others.[1] It is interesting that in none of the clathrates studied was the tetragonal type of packing realized. The small difference in X-ligand geometry on going from NCS^- to NCO^- was sufficient for a transformation of the tetragonal structure to the orthorhombic one. The tetragonal type was realized for the $[CuPy_4(NCO)_2]\cdot 2Py$ clathrate if the tetragonal distortion of the complex occurred at the expense of a lengthening of the axial Cu–NCO bonds. However, from Table 1, it is the *a* parameter parallel to the complex axis that is shortened and the increase of the *c* parameter parallel to the pair of the equatorial Cu–Py bonds may be indicative of a distortion in the equatorial plane.

Our studies of the $[NiPy_4(NCO)_2]\cdot 2Py$ clathrate reveals the main structural features of the title clathrate group. The host complex molecule (Figure 1) has a symmetry of three two-fold axes which coincide with the coordination bonds and are parallel to the unit cell crystallographic axes. The central atom has four pyridine ligands coordinated to it in the equatorial plane which is parallel to the (*bc*) plane. The ligands have a symbiotic arrangement with respect to the equatorial plane, determining a propeller-type conformation. The isocyanate groups coordinated axially lie on the complex axis. However, the strong elongation of the thermal ellipsoids along the *c* parameter indicates that there may be significant deviation of their atoms from the complex axis either due to a small disorder or as a result of thermal motion in this direction.[¶¶]

The guest pyridine molecules reside in the crystal framework cavities (Figure 2) and do not interact with the environment chemically. Each guest molecule lies inside a rectangular parallelepiped with the host nickel atoms lying at the four apices. On the whole, as regards the general packing features the structure is similar to those studied previously.[8–12] As can be seen from the Table 1, the structure parameters are capable of 'breathing' on going from one host complex to another. The largest changes occur in the *a* parameter which is parallel to the complex axis and to the direction of the channel containing the guest species (*cf.* Table 1 and Figure 2). As follows from this

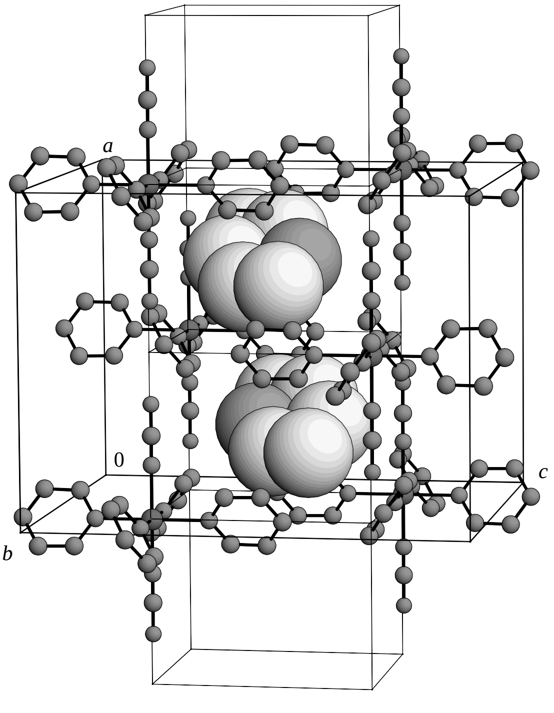

Figure 2 The arrangement of the guest molecules (van der Waals radii) in the rectangular-prismatic channel in the $[NiPy_4(NCO)_2]\cdot 2Py$ clathrate structure. H atoms are omitted. For clarity, the channel boundaries are depicted by thin lines and the unit cell is shown.

[‡] Single crystals of clathrates with linear dimensions from 0.3 to 0.5 mm were mounted in Lindemann glass capillary tubes with a drop of the respective supernatant fluid and the tubes flame-sealed. The search for reflections was performed directly on a diffractometer (λCuKα, graphite monochromator, $\omega/2\theta$-scan). The unit cell parameters were preliminary determined from 25 reflections found in the θ-range 10–15°; checked and refined using 25 to 50 more reflections in the θ-range 15–25°. The space group was determined from the absences which were revealed both from this random data set and by measuring several tens of low index reflections. The crystal of the Zn-clathrate was taken at below +10 °C and instantaneously frozen to –123 °C (150 K). Accurate determination of the symmetry and space group in this case was not possible because of the poor crystal.

[§§] *Crystal data.* Intensities of 1835 independent reflections (1413 data with $I > 0$) were measured on a CAD-4 diffractometer (θ-range 2–78°). The structure was solved by the Patterson and Fourier methods (SHELX-86). Refinement was performed on F^2 (SHELX-93); all data with positive intensities were involved. Non-hydrogen atoms were refined anisotropically. H atoms fixed in calculated positions were refined isotropically. The final value $R = 0.079$ for 1413 reflections and 104 parameters [for 990 reflections with $I > 2\sigma(I)$ $R = 0.053$]. Tables have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1997, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/18.

[¶¶] Attempts to allow a disorder of the isothiocyanate group in the course of the structure solution and refinement resulted in the loss of the solution stability. An analogous situation was observed earlier for the axial nitrate in the structures $[NiPy_4(NO_3)_2]\cdot 2Py$[9] and $[CuPy_4(NO_3)_2]\cdot 2C_6H_6$ (supplementary to ref. 2).

work, the magnitude of the *a* parameter is strongly dependent not only on the X ligand but also on the central atom of the complex.

Thus, the seven title compounds are to be classified as clathrates of the general formula $[MPy_4(NCO)_2]\cdot 2Py$. All of them belong to the orthorhombic type crystallizing in the *Ccca* space group. Among the known $[MPy_4X_2]\cdot 2Py$ compounds, this is the longest row of isostructural clathrates with the same X ligand in the host complex.

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