Clathrates of the [Cu(pyridine)$_4$(NO$_3$)$_2$]

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The clathrate nature of the compounds in the series [M(py)$_4$X$_2$]·2py (py = pyridine) is proved chemically by substituting non-bonded pyridine in [Cu(py)$_4$(NO$_3$)$_2$]·2py using benzene, tetrahydrofuran and chloroform.

The supramolecular nature of MX$_2$·6py† compounds has attracted a great deal of interest as many of these compounds were originally described as 'hexapyridine metal complexes, [M(py)$_6$]X$_2$' and only recent X-ray studies allowed them to be classified as supramolecular compounds of tetrapyridine complexes and pyridine, [M(py)$_4$X$_2$]·2py.[1,2] At present, over 20 compounds with this composition are known and have been shown to be supramolecular. There are grounds for extending this interpretation to other compounds.[1]

Also, these compounds are structurally similar to the Schaeffer's clathrates.[3] In these clathrates the hosts are the complexes, *trans*-[MA$_4$X$_2$] with various substituted pyridines as the A-ligand (complexes with 39 A are reported in the literature[4]). At the same time, complexes where A is the pyridine itself were believed not to form clathrates.[4]

X-Ray crystallography and spectroscopic studies[1,5,6] indicated unambiguously that there are two chemically non-equivalent types of pyridine in the compounds [M(py)$_4$X$_2$]·2py: *a ligand pyridine* coordinated to the host central atom and *a free pyridine* which is chemically non-bonded. However, this evidence alone is insufficient to

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† M = metal(II), X = univalent acidogroup, py = pyridine.

Table 1 Colour and analytical results for the synthesized compounds (standard deviation).

Compound	Colour	Cu (%)		py (%)	
		Found	Calculated	Found	Calculated
$[Cu(py)_4(NO_3)_2]$	violet-lilac	12.55(5)	12.61	61.9(4)	62.8
$[Cu(py)_4(NO_3)_2]\cdot 2py$	blue	9.55(5)	9.60	71.1(5)	71.6
$[Cu(py)_4(NO_3)_2]\cdot 2CHCl_3$	violet-lilac	8.41(7)	8.56	41.9(4)	42.6
$[Cu(py)_4(NO_3)_2]\cdot 2C_6H_6$	dark-blue	9.85(9)	9.62	48.3(7)	47.9
$[Cu(py)_4(NO_3)_2]\cdot 2C_4H_8O$	blue	9.87(4)	9.80	48.5(6)	48.8

unambiguously classify these supramolecular compounds as clathrates whose guest component can be either partially removed or replaced by a chemically different guest with the clathrate host framework being preserved.

The aim of the present work was to provide a chemical proof of the clathrate nature of the compounds $[M(py)_4X_2]\cdot 2py$ by substituting the non-bonded pyridine by other organic components. It should be noted that in the clathrates of complex compounds the stability of the host clathrate framework is determined not only by the geometrical characteristics of the framework and the guests it includes but also by the stability of the host molecule itself.[7] Thus in the compounds $[M(py)_4(NO_3)_2]\cdot 2py$ (M = Zn, Cd) the complete replacement of the non-bonded pyridine is hardly possible, the corresponding tetrapyridine complexes being unstable to such an extent that prevents their isolation as individual phases.[8] Therefore, the pyridine compound chosen for our investigations, $[Cu(py)_4(NO_3)_2]\cdot 2py$, was that of a stable complex. The starting complex was prepared in two steps:[‡]

$$Cu(NO_3)_2\cdot 3H_2O + 6py \xrightarrow{\text{acetone}} [Cu(py)_4(NO_3)_2]\cdot 2py\downarrow + 3H_2O$$

$$[Cu(py)_4(NO_3)_2]\cdot 2py_{\text{solid}} \longrightarrow [Cu(py)_4(NO_3)_2]_{\text{solid}} + 2py_{\text{gas}}$$

The pyridine compound, $[Cu(py)_4(NO_3)_2]\cdot 2py$, was obtained by saturating the complex with pyridine vapours in a desiccator. The chloroform clathrate, $[Cu(py)_4(NO_3)_2]\cdot$ $\cdot 2CHCl_3$, was obtained as octahedral crystals upon isothermal evaporation of a saturated solution of the complex in chloroform. Clathrates with benzene or tetrahydrofuran were obtained by allowing the solid complex to interact directly with the liquid guest.[§]

The colour of the resulting compounds and the analytical data[¶] are summarized in Table 1. It can be seen that in all of the compounds for every mole of the complex there are two moles of the included substance. Since all the syntheses were purposefully carried out with an excess of the included substance, the resulting compositions correspond to the limiting stoichiometry, *i.e.* full occupancy of the cavities. The colour variation of the complex with the change of the included component indicated that changes take place in its molecular structure associated with changes in the packing character of these supramolecular phases.

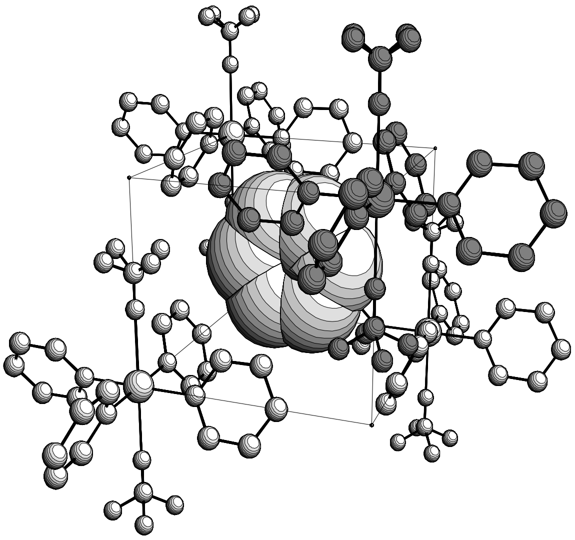

Figure 1 The nearest environment of a guest benzene molecule (van der Waals dimensions) in the $[Cu(py)_4(NO_3)_2]\cdot 2C_6H_6$ clathrate. For clarity, one of the host molecules is darkened; H atoms are not depicted.

In the structure of $[Cu(py)_4(NO_3)_2]\cdot 2C_6H_6$ [††] the benzene molecule is in an environment similar to that in the

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[‡] *Procedure*: $Cu(NO_3)_2\cdot 3H_2O$ (2.42 g, 0.01 mol; analytically pure grade) was dissolved in 20 ml acetone (of special purity grade) with the addition of 4–5 drops of concentrated nitric acid. To the resultant bright-blue solution was gradually poured a mixture of 5 ml acetone and 5 ml (0.062 mol) pyridine (pure). After the reaction was complete the blue precipitate of $[Cu(py)_4(NO_3)_2]\cdot 2py$ was separated from the colourless solution on a glass filter, washed twice with acetone and exposed to air for decomposition with occasional stirring. The final product was violet-lilac. The pyridine odour indicates that the decomposition was not yet complete whereas the appearance of seeds of the light-blue phase of tripyridine complex indicated that $[Cu(py)_4(NO_3)_2]$ had begun to decompose and the drying was stopped immediately. The complex was stored in a tightly closed can. Yield 4.85 g (96% based on copper nitrate).

[§] *Synthesis of* $[Cu(py)_4(NO_3)_2]\cdot 2C_6H_6$: $[Cu(py)_4(NO_3)_2]$ (4.4 g, powder) was stirred with 50 ml of benzene. The mixture was heated for 10 min to 50–60 °C and left to cool with stirring. The clathrate was separated from the mother liquor, dried in air for several seconds and then stored in a desiccator under an atmosphere of benzene. Yield 5.3 g (90%).

[¶] The analysis for Cu was performed by complexometric titration with 0.01 M EDTA using pyrocatechin violet as indicator. Pyridine was determined potentiometrically by reverse titration with 0.4 M KOH solution. Excess of nitric acid (0.4 M) was used for sample neutralization. Three or more determinations were performed in each case.

[††] *Crystal data.* Crystals of the $[Cu(py)_4(NO_3)_2]\cdot 2C_6H_6$ clathrate were obtained by recrystallization of the $[Cu(py)_4(NO_3)_2]$ complex from a benzene–methanol mixture (1 : 1 by volume). The crystals are tetragonal with $a = 11.100(1)$, $c = 12.921(1)$ A, $V = 1592(1)$ A^3, $Z = 2$, $D_c = 1.38$ g cm^{-3}, space group I422. The unit cell parameters and intensities of 1833 reflections (529 unique data, $R_{\text{int}} = 0.024$) were measured on a KM-4 four-circle diffractometer (graphite monochromated λCuK_α, $\omega/2\theta$-scan, $2\theta_{\max} = 156°$). The structure was solved by Patterson and Forier methods using SHELXL-93. The hydrogen atoms were fixed at calculated positions. Refinement on F^2 was performed anisotropically for all non-hydrogen atoms. The final value $R = 0.047$ ($R_w{}^2 = 0.125$, $S = 1.06$) for all 529 independent data and 63 parameters. The final 'Flack' parameter for the absolute structure $x = -0.01(8)$. The central atom of the host complex occupies position 422; the Cu–N$_{\text{py}}$ bonds are aligned along the two-fold axes. The four-fold axis coincides with the axis of the complex, with the pair of the terminal nitrate group oxygens being disordered in two positions. The Cu–N$_{\text{py}}$ distance is 2.029(3) A and the Cu–O$_{\text{nitrate}}$ distance is 2.468(5) A. Full lists of bond angles, bond lengths, atomic coordinates and thermal parameters 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 1135/11.

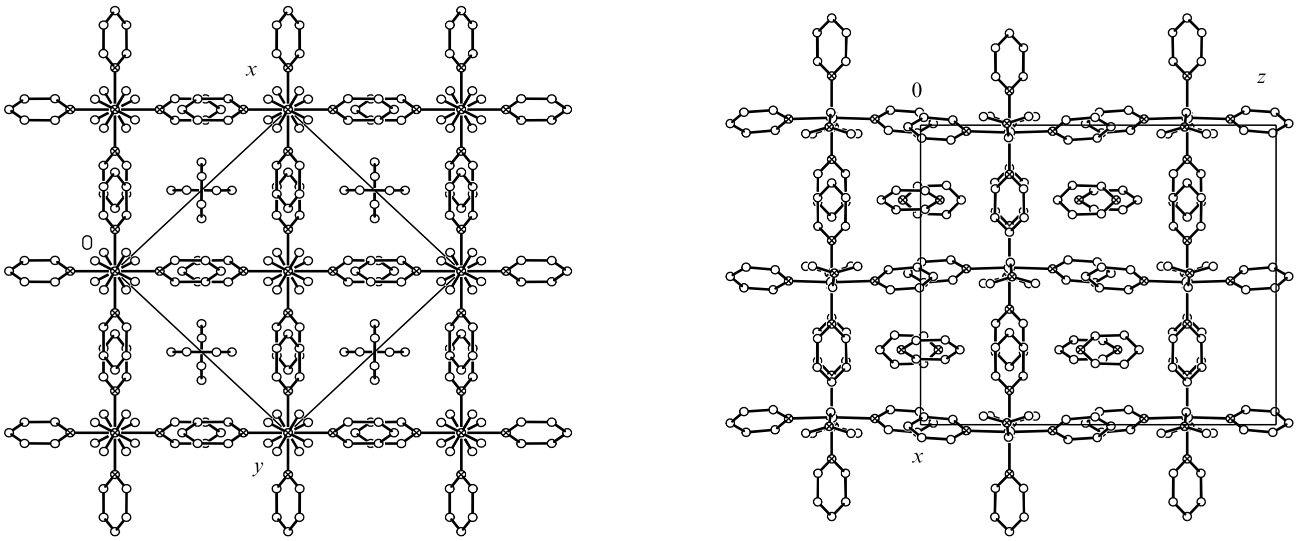

Figure 2 Structure projections of the $[Cu(py)_4(NO_3)_2]\cdot2C_6H_6$ clathrate along the *c* axis (left) and the $[Cu(py)_4(NO_3)_2]\cdot2py$ clathrate[9] along the *b* axis (right).

compounds in the series $[M(py)_4X_2]\cdot2py$ (Figure 1). The molecule is included into a rectangular parallelepiped at the four appices of which, arranged in tetrahedrally distorted fashion, are located the central atoms of the molecules of the complex. The height of the parallelepiped, 6.45 A, is equal to half the *c* parameter and the sides of the base which, in this case, have the same length, are half the length of the diagonal of the tetragonal unit cell base. The recently reported structural data for the pyridine compound $[Cu(py)_4(NO_3)_2]\cdot2py$ (full structure at 173 K[9] and the room temperature unit cell parameters[1]) allow a comparison between these two clathrates. In the pyridine clathrate crystallizing in the orthorhombic system the host framework has practically the same structure although there are some distortions. For instance, the nitrate group noticeably deviates from the complex axis. The height of the parallelepiped accomodating the guest pyridine molecule is 6.26 A and the base dimensions are 7.40×8.45 A. In spite of these differences and the differences in the crystallographic parameters the two clathrates can be considered to be isomorphous; their structural similarity is demonstrated in Figure 2 showing projections of the two structures along the crystallographic directions parallel to the complex axis.

Thus the non-bonded pyridine in $[Cu(py)_4(NO_3)_2]\cdot2py$ can be easily replaced by its nearest geometrical analogue, benzene, in spite of the substancial differences in the chemical nature between these organic components. The clathrate phase of $[Cu(py)_4(NO_3)_2]$ is preserved with only slight distortions occurring when it 'adjusts' to a particular guest. The composition of the other compounds, with tetrahydrofuran and chloroform, allows us to expect that they have a similar structure. This conclusion is also favoured by the fact that clathrates of this complex could not be obtained with the more bulky substituted benzenes (toluene, xylenes) which obviously cannot be accommodated into the cavities of such type of structure.

The results obtained suggest that the unsuccessful attempts to replace the non-bonded pyridine in other compounds of this type, for example $[Zn(py)_4(NO_3)_2]\cdot2py$,[10] are explained by the insufficient stability of the complex itself rather than by the 'poor' geometry of the clathrate phase. It appears that only a partial substitution is possible in such cases.

Possibly, the chemical proof of the clathrate nature for $[Cu(py)_4(NO_3)_2]\cdot2py$ allows the clathrate classification to be extended to all isomorphous compounds with the general formula $[M(py)_4X_2]\cdot2py$ and we may expect that in the near future a series of new clathrates of this type with guests other than pyridine will be obtained.

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References

1 D. V. Soldatov and J. Lipkowski, *Zh. Strukt. Khim.*, 1995, **36**, 1070 (*Russ. J. Struct. Chem.*, 1995, **36**, 979).
2 D. V. Soldatov, *J. Inclusion Phenom.*, 1995, **20**, 191.
3 W. D. Schaeffer, W. S. Dorsey, D. A. Skinner and C. G. Christian, *J. Am. Chem. Soc.*, 1957, **79**, 5870.
4 J. Lipkowski, in *Organic Crystal Chemistry*, Oxford University Press, Oxford, 1991, p. 27.
5 D. V. Soldatov, J. Lipkowski and E. V. Grachov, *Zh. Strukt. Khim.*, 1995, **36**, 912 (*Russ. J. Struct. Chem.*, 1995, **36**, 830).
6 D. V. Soldatov and J. Lipkowski, *Zh. Strukt. Khim.*, 1995, **36**, 1074 (*Russ. J. Struct. Chem.*, 1995, **36**, 983).
7 Yu. A. Dyadin and N. V. Kislykh, *Mendeleev Commun.*, 1991, 134.
8 Yu. A. Dyadin, D. V. Soldatov, V. A. Logvinenko and J. Lipkowski, *J. Coord. Chem.*, 1996, **37**, 63.
9 G. Beurskens, C. F. Martens, R. J. M. Nolte, P. T. Beurskens and J. M. M. Smits, *J. Chem. Crystallogr.*, 1995, **25**, 425.
10 D. V. Soldatov, V. A. Logvinenko and Yu. A. Dyadin, *Zh. Neorg. Khim.*, 1995, **40**, 324 (*Russ. J. Inorg. Chem.*, 1995, **40**, 309).

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