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On the Composition of the Orthorhombic Clathrates of Tetrapyridine-metal(II) Complexes with Pyridine

Letter to the Editor

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The versatile clathration ability of $[MA_4X_2]$ complexes (M is a metal(II), A is a substituted pyridine, and X is a univalent anion) is well known [1]. More dramatic changes in the type of clathrate structure and the host/guest ratio occur when the neutral ligand A is varied. It is thus interesting to study the host properties of the complexes containing unsubstituted pyridine, $[MPy_4X_2]$ (Py=pyridine). For some years these complexes seemed to form no clathrates. It has recently been revealed that this is not the case; many of the complexes form clathrates of a new structural type (orthorhombic, *Ccca*) with pyridine as a guest, $[MPy_4X_2] \cdot 2Py$ [2]. The most interesting fact is that some of the structures determined by X-ray crystallography were not classified as inclusion compounds [3,4]. Ito *et al.* [5] were the first to describe the $[CdPy_4I_2] \cdot 2Py$ compound studied by them as a clathrate.

Recently Selkti *et al.* reported the crystal structure of one such compound, '$[CuPy_4Br_2] \cdot Py$' [6]. The accuracy of the X-ray experiment is beyond doubt. Nevertheless, the host : guest composition of 1 : 1 established only from an X-ray study is very dubious. Many clathrates of analogous $[MPy_4X_2]$ hosts possessing the same symmetry and similar unit cell dimensions have a 1 : 2 host-to-guest mole ratio. This composition applies to a number of clathrates with Cd, Ca, Co, Cu, Mg, Ni, Zn as M and Br, I, NO_2, NO_3, HCOO as X in the host complex [2]. Moreover, in contrast to the well known β-phases, where the guest content may vary [1], the $[MPy_4X_2] \cdot 2Py$ orthorhombic clathrates have a constant composition. This results from a large amount of the guest and the structural peculiarities of the host framework. The constancy of the composition for $[ZnPy_4(NO_3)_2] \cdot 2Py$ was demonstrated by a special phase investigation [7].

The doubt about '$[CuPy_4Br_2] \cdot Py$' may be readily solved by a simple recalculation. One quarter of the host and a half of the guest molecules form the independent part of the structure. Taking into account the symmetry in the *Ccca* space group, the number of molecules per unit is:

for host $1/4 \times 16 = 4$, for guest $1/2 \times 16 = 8$.

Therefore the true formula should be written as $[CuPy_4Br_2] \cdot 2Py$, with $m_r = 698$ and $\mu_{cal} = 342.1\ mm^{-1}$.

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