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Crystal Structure of the Clathrate Compound [Dibromotetra(pyridine)copper(II)] · Pyridine. Characterization by EXAFS of the Pyridine Desorption Product

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Abstract. Powder samples of the new compound $[Cu(C_5H_5N)_4 \cdot Br_2](C_5H_5N)$ and of its desorption product have been studied by EXAFS. The crystal structure of $[Cu(C_5H_5N)_4Br_2] \cdot (C_5H_5N)$ has been determined from three-dimensional X-ray diffraction data and refined to the R value 0.038 for 379 observed reflections. (Orthorhombic, *Ccca*, $a = 12.033(8)$, $b = 14.764(3)$, $c = 16.768$ Å, $V = 1897(3)$ Å^3, $Z = 4$). The copper atom lies on a 222 symmetry site and is hexacoordinated with four nitrogen and two bromine atoms, forming an elongated octahedron with the bromine atoms in apical positions (Cu-Br distance: 3.201(2) Å, Cu-N1/N2 distances: 2.02(1)/2,07(1) Å). The host molecules $(Cu(C_5H_5N)_4Br_2)$ form layers parallel to the (001) plane. Cavities in the space between these layers, bound by pyridine ligands protruding into this space, are occupied by the guest molecules (C_5H_5N). The guest desorption at room temperature is accompanied by a chemical and structural destruction of the host, leading to the known compound $Cu(C_5H_5N)_2Br_2$.

Supplementary Data relevant to this article (lists of observed and calculated structure factors, calculated positional parameters of H atoms, root-mean-square amplitudes of thermal vibration and anisotropic thermal parameters) have been deposited with the British Library as Supplementary Publication SUP 82163 (5 pages).

Key words: Crystal structure, EXAFS, clathrate, 4-pyridine, 2-pyridine, Cu(II).

1. Introduction

The present investigation was undertaken during research on gel formation in pyridine-inorganic halide systems in the presence of macrocyclic molecules.

The title compound belongs to the $[MA_4X_2] \cdot G$ clathrate family with Cu(II)Py$_4$-Br$_2$ as host and a pyridine molecule (Py) as guest, in a 1 : 1 ratio (M: transition metal(II), A: neutral ligand, X: anionic ligand, G: guest). Many crystal structures of this inclusion compound type with methyl-Py as the neutral ligand are known [1–3], but only a few complexes with unsubstituted pyridines and halogen or pseudohalogen atoms as anionic ligand have been described. The reported structures of

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tetrakis(pyridine)metal(II)halides show that in most cases the molecular packing is not appropriate to accept a guest molecule [4–8].

2. Experimental

A blue compound (**I**) precipitates when dissolving solid copper(II)dibromide salt in dry pyridine. A green decomposition product (**II**) is obtained spontaneously from **I** standing in air at room temperature; the evolution is complete after 6 h. As a consequence of such an instability of **I** chemical analysis did not lead to reliable results, the formula $Cu(C_5H_5N)_4Br_2 \cdot (C_5H_5N)$ was then established from an X-ray study on single crystals after crystallization of **I**. The weight loss measurement from the established formula pointed to the formula $Cu(C_5H_5N)_2Br_2$ for compound **II**, corresponding to the loss of the three pyridine molecules (chemical analysis, C: 31.4%; N: 7.16%; H: 4% for calculated values 30.7%, 7.16% and 5%).

2.1. EXAFS ANALYSIS

EXAFS (Extended X-ray Absorption Fine Structure) is the only technique that provides stuctural information: the local average structure around an X-ray absorbing atom, which can be applied to amorphous as well as crystallized compounds, or solutions. EXAFS analysis was performed on transmission absorption spectra of **I** and **II**. Data were recorded on the same powdered sample before and after desorption, at the copper K_α absorption edge (room temperature), using the EXAFS-I station of LURE (the French synchrotron radiation facility) under standard operating conditions of the storage-ring DCI.

2.2. X-RAY DIFFRACTION

Microcrystals of **I** were left for six months in the mother liquor at room temperature in order to grow a crystal. A summary of crystal data, data collection parameters and structural refinement are presented in Table I. Diffraction data were collected on a crystal sealed within a thin-walled Lindeman glass capillary. The data were strongly affected by absorption, a double correction was necessary, the first based on Ψ scans of top reflections [9] and the second using the DIFABS [10] program. The structure was solved by the heavy atom method. The H atoms were located at geometrically calculated positions and allowed to ride on their parent C atoms during the refinements with a fixed isotropic temperature factor. The few residual peaks on the last difference synthesis were close to the copper and bromine atoms. The final positional and equivalent isotropic thermal parameters are listed in Table II.

Four X-ray powder diffraction data sets of **II** were collected with a Seifert vertical diffractometer powered by an Enraf-Nonius generator (40 kV and 10 mA with CuK_α radiation). The sample was scanned over the 3–60° range in 2θ

TABLE I. X-ray diffraction experimental details.

Crystal data	
$[Cu(C_5H_5N)_4Br_2] \cdot (C_5H_5N)$	$Mr = 618.9$
Orthorhombic	*Ccca*
$a = 12.033(8)$ Å	$\alpha = 90°$
$b = 14.764(3)$ Å	$\beta = 90°$
$c = 16.768(5)$ Å	$\gamma = 90°$
$Z = 4$	
$V = 1897(3)$ Å^3	$\delta_{cal} = 1.38$ g cm^{-3}
MoK_α ($\lambda = 0.71073$ Å)	Cell parameters from 25 reflections ($\theta = 8$–$12°$)
$\mu_{cal} - 341.04$ mm^{-1}	$T = 295$ K
blue	prismatic ($0.40 \times 0.20 \times 0.20$ mm)
Data collection	
Enraf-Nonius CAD4 Diffractometer	$\omega/2\theta$ Scans
Absorption corrections	
based on scans	$T_{min} = 0.735$ $T_{max} = 0.999$
analytical	$C_{min} = 0.711$ $C_{max} = 1.293$
814 measured reflections	
599 independent reflections	$R_{int} = 0.016$
379 observed reflections	$I_{net} > 3\,\sigma(I_{net})$
$\theta_{max} = 25°$	3 standard reflections
$h_{min} = 0$ $h_{max} = 11$	intensity variation: -1.2%
$k_{min} = 0$ $k_{max} = 14$	
$l_{min} = 0$ $l_{max} = 16$	
Refinement	
H-atom parameters not refined	Refinement on F
$R = S\,\|\|Fo\| - \|Fo_{av}\|\|/S\,\|Fo\| = 0.036$	68 parameters
379 reflections	$\omega R = 0.054$
$GOF = 3.7$	$\omega = 1/(\sigma F)^2 = 4F^2/[\sigma I^2 + (pF^2)^2]^{1/2}$, $p = 0.4$
$(\Delta/\sigma)_{max} = 0.01$	$\Delta\rho_{min} = -0.63$ eÅ^{-3}
	$\Delta\rho_{max} = 0.57$ eÅ^{-3}

Atomic scattering factors from *International Tables for X-ray Crystallography* [11], Tables 2.2B and 2.3.1.

with a step size of 0.02° and a counting interval of 8 s. Rietveld refinements of the bis(pyridine)dibromide structure [12, 13] converged to essentially the same structure with a good data fit ($R_p = \Sigma\,|y_i - y_{ic}|/\Sigma\,y_{iO} = 0.16\%$ and $R_F = \Sigma\,||F_O| - |F_C||/\Sigma\,|F_O| = 0.10\%$ for 374 structure factors).

TABLE II. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) with their estimated standard deviations (starred atoms were refined isotropically).

	x	y	z	B/B_{eq}
Br	−0.2660(1)	0.250	0.250	5.15(4)
Cu	0.000	0.250	0.250	7.6(1)
N(1)	0.000	0.1130(7)	0.250	3.8(3)
N(2)	0.000	0.250	0.1268(7)	4.3(3)
N(3)	0.250	0.500	0.4490(9)	5.5(4)
C(11)	0.080(1)	0.0656(8)	0.2126(8)	3.8(3)*
C(12)	0.0832(9)	−0.0270(7)	0.2112(8)	3.4(3)*
C(13)	0.000	−0.0735(9)	0.250	3.7(3)*
C(21)	−0.083(1)	0.2134(8)	0.086(1)	5.4(2)*
C(22)	−0.086(1)	0.2133(9)	0.002(1)	6.0(3)*
C(23)	0.000	0.250	−0.038(1)	6.2(4)*
C(31)	0.170(1)	0.462(1)	0.4894(8)	5.5(4)
C(32)	0.167(1)	0.461(1)	0.5721(9)	6.3(4)
C(33)	0.250	0.500	0.611(1)	5.7(5)

Note: $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \bar{a}_i \bar{a}_j$.

2.3. PROGRAMS

EXAFS: EXAFS analysis package [14], running on a GOUPIL G5-286 VGA personal computer.

X-ray diffraction on single crystals: Cell refinements and data collection, Enraf-Nonius CAD-4 software. Data reduction, structure resolution and refinements: SDP software [15]. Absorption correction: on Ψ scans [9] and DIFABS [10]. Molecular graphics: SYBYL [16], ORTEP [17].

X-ray diffraction on powder samples: Refinements, Rietveld programs DBWS-9006 [18].

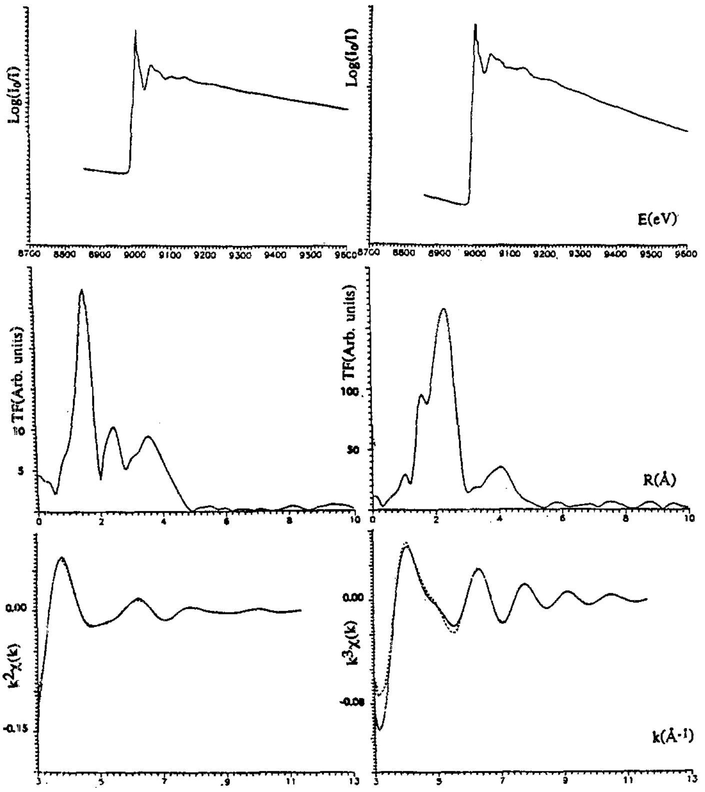
The calculations were performed using a VAX3100.

3. Discussion

3.1. EXAFS ANALYSIS

In a first approach to characterizing the pyridine-copper dibromide system, the study of both compounds was performed by EXAFS [19]. The coordination of copper was best fitted to four nitrogen and two bromine atoms, and two nitrogen and two bromine atoms for compounds **I** and **II**, respectively.

Figure 1 displays the EXAFS oscillations and its Fourier transform (FT) for compound **I**. The first and second peaks correspond to contributions of the pairs Cu-N$_4$ and Cu-Br$_2$ superimposed with that of Cu-C$_8$, respectively. The decrease of



a) b)

Fig. 1. Absorption spectra on CuK_α edge, Fourier transforms and calculated (· · ·) and Fourier filtered experimental (—) plots for (a) [Cu(C_5H_5N)$_4$Br$_2$] · (C_5H_5N); (b) Cu(C_5H_5N)$_2$ · Br$_2$. *Note*: k is the photoelectron wave vector: $k = [(2me/h^2)(E - E_0)]^{1/2}$.

the first peak and the displacement of the second peak towards shorter distances observed in the FT of product **II** (Figure 1b), indicates that the copper coordination is not the same. The fit of parameters is presented in Table III.

These results identify the desorption compound as the known compound: bis(pyridine)dibromide [Cu(C_5H_5N)$_2$Br$_2$] [12, 13].

3.2. X-RAY STRUCTURAL ANALYSIS

Compound **I** presents, as in all known tetrakis (pyridine)metal(II)halide complexes, a molecular structure where the metal coordinates four pyridines and two halogen atoms in trans positions forming an elongated octahedron (Table IV). Distances for the Cu atom and its ligands agree with those found in the previously reported crystallographic study of bis(pyridine)dichloride [12, 21] and bis(pyridine)dibromide compounds [12, 13]. In the latter, the copper also presents a pseudo-octahedral

TABLE III. Fitted parameters with theoretical amplitude and phase parameters [20] for $[Cu(C_5H_5N)_4Br_2] \cdot (C_5H_5N)$ and for its desorption product $Cu(C_5H_5N)_2Br_2$. Starred parameters were fixed during the fitting.

	pairs	N_i	R_i (Å)	R_{xray} (Å)	σ_i (Å)	E_0 (eV)
compound **I**	Cu-N	4*	2.04(2)	2.05(3)	0.08	−4.0
	Cu-C	8*	2.98(4)	2.97(1)	0.10	−0.7
	Cu-Br	2*	3.11(4)	3.201(2)	0.13	7.9
compound **II**	Cu-N	2*	2.01(2)	2.013(5)	0.09	−9.8
	Cu-Br	2*	2.48(4)	2.451(1)	0.09	−13.3

Note: The fitted parameters are: N_i the atom number of the ith shell, R_i the average distance which separates the absorbing atom from these N_i scattering atoms, σ_i the deviation from this distance R_i and E_0 the origin of the energy above which the photoelectron is free.

TABLE IV. Selected bond lengths (Å) and angles (°).

Cu-N(1)	2.02(1)	Cu-N(2)	2.07(1)	Cu-Br	3.201(2)
N(1)-N(2)	2.89(1)	N(1)-Br	3.786(5)	N(2)-Br	3.810(7)
N(1)-C(11)	1.35(1)	N(2)-C(21)	1.33(2)	N(3)-C(31)	1.30(2)
C(11)-C(12)	1.37(2)	C(21)-C(22)	1.40(2)	C(31)-C(32)	1.39(2)
C(12)-C(13)	1.38(1)	C(22)-C(23)	1.35(2)	C(32)-C(33)	1.33(2)

N(1)-Cu-N(2)	90.0	N(1)-Cu-Br	90.0
N(2)-Cu-Br	90.0	N(1)-N(2)-N(1)^{ii}	88.8(4)
N(2)-N(1)-N(2)^{i}	91.2(4)		
N(1)-C(11)-C(12)	123(1)	C(11)-C(12)-C(13)	118(1)
C(11)-N(1)-C(11)^{i}	117(1)	C(12)-C(13)-C(12)^{i}	120(1)
N(2)-C(21)-C(22)	123(2)	C(21)-C(22)-C(23)	118(1)
C(21)-N(2)-C(21)^{ii}	118(1)	C(22)-C(23)-C(22)^{ii}	121(2)
N(3)-C(31)-C(32)	123(1)	C(31)-C(32)-C(33)	118(1)
C(31)-N(3)-C(31)^{iii}	117(1)	C(32)-C(33)-C(32)^{iii}	121(2)

Note: Symmetry codes (i) $\bar{x}, y, \bar{z} + 1/2$; (ii) $\bar{x}, \bar{y} + 1/2, z$; (iii) $\bar{x} - 1/2, \bar{y} + 1, z$.

coordination, but its local structure differs essentially in that the metal is bound by four shared bromine atoms and two pyridines, with two bromines located at a shorter distance (2.451(1) Å) than the others (3.240(1) Å). In compound **I**, the copper (which lies on a symmetry site 222) and the four coordinated nitrogens are strictly coplanar. The metal exhibits a very large anisotropic thermal vibration with the largest amplitude (0.452 Å) perpendicular to the nitrogen plane (Figure 2). Due to this motion, the B_{eq} of the copper is significantly higher than those of other atoms. In the copper environment, the dihedral angle between the planes of two consecutive pyridine ligands are all equal to 75.3° and those between the nitrogen plane and the two crystallographic independent pyridine rings (pyN(1) and pyN(2)) 57.4° and 61.9° respectively.

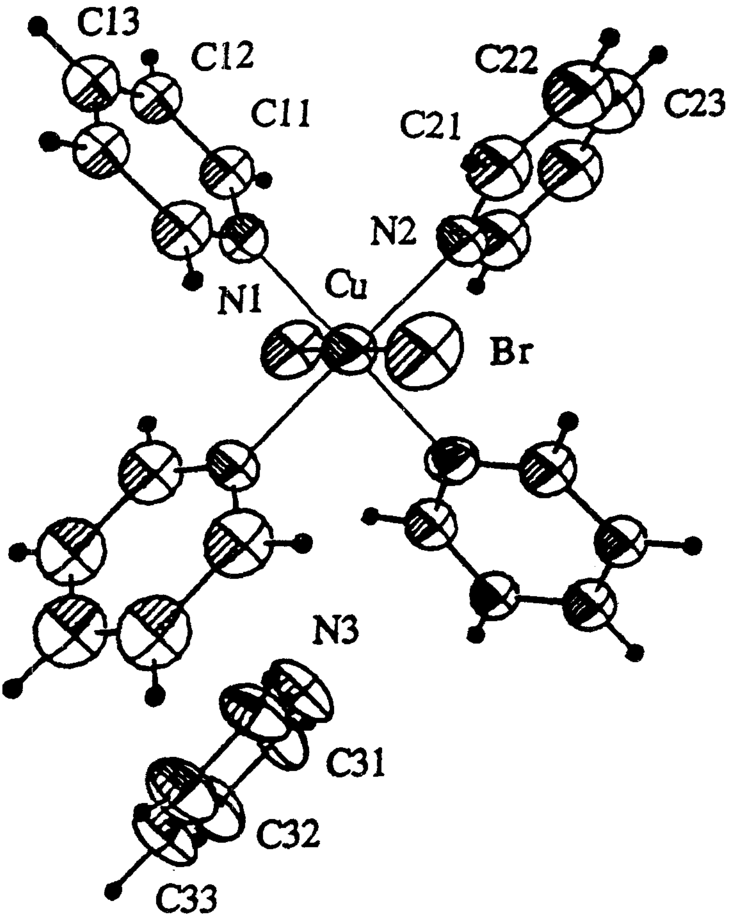


Fig. 2. ORTEP view of $[Cu(C_5H_5N)_4Br_2] \cdot (C_5H_5N)$.

The crystal packing may be described as built from layers of host molecules parallel to the (001) plane with the Br-Cu-Br axis along the [1 0 0] direction (Figure 3). The guest molecules are located in cavities formed by pyridine ligands (PyN(2)) protruding into the space between the host layers. Consequently, in this space, there are only pyridine molecules. Channels extending along the [1 0 0] direction contain columns of parallel guest, while along the [0 1 0] direction, channels contain columns of twisted guest pyridines (twist angle between consecutive pyridines: ±60.5°). In both directions, each cavity is bound by two columns of bromine atoms and four stacks of pyridine ligands shared by the neighbouring channels. Differences are observed between the thermal parameters and the Cu-N distances of the two coordinated pyridines. The largest values correspond to PyN(2), the pyridine located in the 'pyridine layer'.

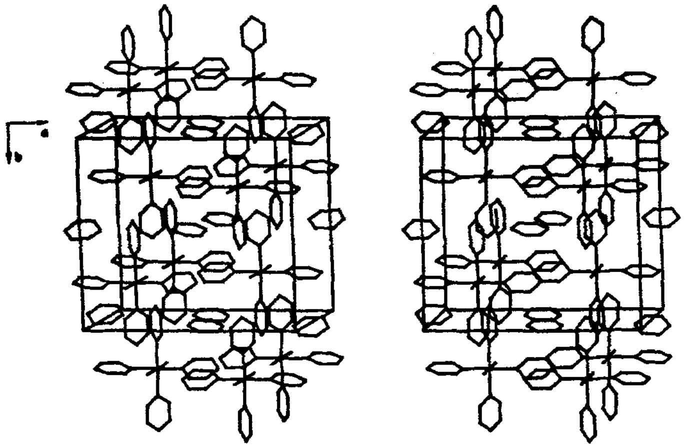


Fig. 3. SYBYL stereoscopic view along the [1 0 0] direction of the $[Cu(C_5H_5N)_4Br_2] \cdot (C_5H_5N)$ structural packing.

X-ray powder diffraction of **II** supports the EXAFS results concerning the identity of the $Cu(C_5H_5N)_2Br_2$ compound [12, 13].

4. Concluding Remarks

This work indicates that, standing in air and at room temperature, the guest desorption of **I** is accompanied by a chemical and structural destruction of the host. The pyridine desorption concerns not only the guest molecules but also two other pyridines directly coordinated to the metal. The thermal parameters of both pyridine ligands in **I**, point out that the PyN(2) would be lost preferentially, together with the guest molecules, during the desorption.

To reach the octahedral coordination of copper a polymeric structure is formed by sharing two bromine atoms. The product is $Cu(C_5H_5N)_2Br_2$, a known material because of its magnetic properties.

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