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J Chem Crystallogr (2008) 38:413–417
DOI 10.1007/s10870-008-9323-0



ORIGINAL PAPER

# Synthesis, Crystal Structure and Spectroscopy of *catena*-poly-bis(azido-*N1,N1*)(2-Aminopyrimidine)Copper(II)

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Received: 5 October 2007 / Accepted: 8 January 2008 / Published online: 26 January 2008


**Abstract** The compound $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$ (ampym = 2-aminopyrimidine) has been synthesized and characterized by X-ray crystallography and infrared spectroscopy. In addition, Ligand Field and powder EPR measurements have been performed. The structure is solved in space group P21/c with $a = 7.303(2)$, $b = 19.716(4)$, $c = 5.949(1)$ Å, $\beta = 98.17(3)$, $V = 847.9(3)$ Å$^3$, $Z = 2$ with final R = 0.0382. The coordination geometry around the Cu(II) ion is distorted square pyramidal, with four nitrogen atoms of four bridging azido anions in the basal plane with Cu–N distances that range from 1.998(3) to 2.069(3) Å. The apical position is occupied by a nitrogen atom of the ampym molecule at a Cu–N distance of 2.169(3) Å. The trans-basal angles are 165.7(1) and 143.9(1)°. Weak hydrogen bonding is observed between the two amine hydrogen atoms and nitrogen of an azide anion and the pyrimidine-ring nitrogen atom of a neighbouring molecule (N···N distances 3.174(5), 3.106(4) Å). These last hydrogen bonds (N7···N3) are forming so-called "Watson-Crick type" hydrogen bonds. In the infrared the vibrations of the coordinated azide anion are observed at 2,062, 1,273 and 655 cm$^{-1}$, while the Cu–N vibrations are observed at 370 and 224 cm$^{-1}$. Ligand-field and EPR spectra are uneventful and give spectral parameters expected in the range for such Cu(II) compounds. Magnetic susceptibility measurements reveal a weak antiferromagnetic interaction between the Cu(II) ions.

**Keywords** Copper · 2-Aminopyrimidine · Azide · Infrared · Hydrogen bonding

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## Introduction

The ligand used in this study, 2-aminopyrimidine (abbreviated as ampym), is of particularly interest for structural and magnetic studies of metal complexes and has been of interest, specially for Cu(II) compounds [1, 2]. Different Cu(II) compounds with ampym were investigated by X-ray crystallography depending on the nature of the anion and the synthetic method. With halides as anions mononuclear and polymeric compounds have been obtained in which ampym acts as a monodentate or a bidentate ligand [3–6]. With other anions like sulphate [7], triflate [8], nitrate [9] and dicyanamide [10], mononuclear or polynuclear Cu(II) compounds are obtained, all with ampym acting as a monodentate ligand. X-ray structures of a dinuclear methoxido-bridged Cu(II) [1, 11] and a hydroxido-bridged Cu(II) compound [12] were also obtained, again with ampym acting as a monodentate ligand. With tetrafluoridoborate as an anion surprisingly a very complicated trinuclear-based polymeric structure was obtained [13]. It should also be mentioned that the ligand ampym is known to be useful as a starting material for template synthesis with Cu(II) triflate, forming completely new organic compounds [14, 15], in which solvent additions have taken place.

The azide ion is known to be a versatile ligand for generating bridging systems and the amount of studies concerning these types of compounds is really impressive

[2]. The azide ion can act as a monodentate or as a bridging ligand in two different ways, the end-on mode and end-to-end mode [16–19]. With ampym and the azide anion some years ago a polymeric trinuclear-based compound was reported, i.e. $[Cu_3(ampym)_2(\mu_{1,1}\text{-}N_3)_4(\mu_{1,3}\text{-}N_3)_2(dmf)_2]_n$ [2].

In this study, we present the molecular and lattice structure, and some spectroscopic and magnetic properties of the polynuclear compound $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$. Contrary to earlier reported azide-bridged compounds, in this case only a weak antiferromagnetic interaction is observed. In the literature only a few similar types of compounds were found, of which the X-ray crystal structure was published, i.e. $[Cu(2\text{-chloropyrimidine})(\mu_{1,1}\text{-}N_3)_2]_n$ [20] and $[Cu(3,4\text{-lutidine})(\mu_{1,1}\text{-}N_3)_2]_n$ [21].

## Experimental

### General and Physical Methods

C, H, N determinations were performed on a Perkin-Elmer 2400 Series II analyser. UV–Vis spectra were obtained on a Perkin-Elmer Lambda900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Bruker-EMX*plus* spectrophotometer (field calibrated by DPPH, $g = 2.0036$). FTIR spectra were obtained on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4,000–300 $cm^{-1}$, res. 4 $cm^{-1}$). Far-IR spectra were recorded on a Bruker 113v spectrophotometer as polyethylene pellets (500–100 $cm^{-1}$, res. 2 $cm^{-1}$). Magnetic susceptibility measurements (5–300 K) were carried out (at 0.1 T) using a Quantum Design MPMS-5S SQUID magnetometer. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

### Synthesis

The ligand ampym was used as commercially available and applied without further purification. Synthesis of the compound: 0.36 g (1 mmol) $Cu(CF_3SO_3)_2$ and 0.10 g (1 mmol) ampym were both dissolved in 15 ml methanol. The ligand solution was added carefully to the copper solution. Then 0.06 g (1 mmol) sodium azide dissolved in about 1 ml of water was added dropwise while stirring the solution. The solution was filtered to remove any non-dissolved material and was left standing in the open air. After a day, very dark brown small needle-shaped crystals were formed. They were collected, washed with the mother liquid and dried. Yield about 82%. Elemental analysis for $C_4H_5CuN_9$: [found(calc.)]: C 19.7 (19.8)%; H 2.1 (2.1)%; N 51.7 (51.9)%.

### X-ray Crystallography

A suitable crystal was selected from the mother liquid and mounted to a glass fibre using the oil-drop method; data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated MoK$\alpha$ radiation). The intensity data were corrected for Lorentz and polarization effects, for absorption and extinction. The structure was solved by direct methods. The programs COLLECT [22], SHELXS-97 [23], SHELXL-97 [24] were used for data reduction, structure solution and structure refinement, respectively. Refinement of $F^2$ was done against all reflections. All non-hydrogen atoms were refined anisotropically. All H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data are presented in Table 1.

## Results and Discussion

### Description of the Crystal Structure

A plot showing the numbering scheme of the title compound is presented in Fig. 1, and selected bond distances and angles are given in Table 2. The coordination geometry of the Cu(II) atom is distorted square pyramidal. The basal plane is formed by four nitrogen atoms of four bridging azido anions at Cu–N distances that range from 1.998(3) to 2.069(3) Å. The apical position is occupied by a nitrogen atom of the ampym molecule at a Cu–N distance of 2.169(3) Å. The trans-basal angles are 165.7(1) and 143.9(1)°.

The distortion of the copper coordination polyhedron from square pyramidal can be best described by the structural parameter $\tau$ ($\tau$ describes the relative amount of trigonality; $\tau = 0$ corresponds to for square pyramidal geometry and $\tau = 1$ to trigonal bipyramidal) [25]. For the title compound, $\tau = 0.36$ indicating a quite large distortion from an ideal square pyramid towards trigonal bipyramidal. The Cu–Cu distance in the chain is 3.103(3) Å.

The above-mentioned distances and Cu(II) coordination geometry are resembling those found for the compound $[Cu(2\text{-chloropyridine})(N_3)_2]_n$ [20], that compound has also a large distortion from square pyramidal ($\tau = 0.41$). However, the title compound has all four short bonds to the azide anions, contrary to the two compounds in the literature, which have a short and a long bond to the bridging azide anions [20, 21].

**Table 1** Crystallographic data for $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$

| | |
|---|---|
| Formula | $C_8H_{10}Cu_2N_{18}$ |
| CCDC deposit no | CCDC-661738 |
| Molecular weight | 485.42 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| $a$ (Å) | 7.303(2) |
| $b$ (Å) | 19.716(4) |
| $c$ (Å) | 5.949(1) |
| $\beta$ (°) | 98.17(3) |
| $V$ (Å$^3$) | 847.9(3) |
| Z | 2 |
| $D_{calc}$ (g/cm$^{-3}$) | 1.901 |
| $F$(000) | 484 |
| $\mu$ (cm$^{-1}$) | 2.550 |
| Crystal size (mm) | 0.30 × 0.30 × 0.20 |
| Temperature (K) | 173(2) |
| $\theta$ min, $\theta$ max (°) | 2.07, 27.58 |
| Total reflections | 12,510 |
| Total unique reflections | 1,946 ($R_{int}$ = 0.0745) |
| No. of refined data, parameters | 1,946, 127 |
| $R^a$, $wR2^b$, $S^c$ | 0.0382, 0.1237, 1.167 |
| Min. and max. resd. dens. (e/Å$^3$) | −1.143, 0.524 |

[a] $R1 = \sum||F_o|-|F_c||/\sum|F_o|$

[b] $wR2 = \left[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right]^{1/2}$

[c] Goodness-of-fit $S = \left[\sum w(F_o^2 - F_c^2)^2/(n-p)\right]^{1/2}$ where $n$ is the number of reflections and $p$ the number of parameters

The lattice structure is stabilized by stacking between the pyrimidine groups (Shortest Ring–Ring distances of 3.65 Å) and by hydrogen bonding of which one H bond is from the amine hydrogen atom to a nitrogen atom of a coordinated azide nitrogen (N···N distance 3.174(5) Å). The other H bond is from the other N–H to a pyrimidine nitrogen of a neighbouring molecule (N···N distances 3.106(4) Å). The last hydrogen bonds are forming a so-called "Watson-Crick" type hydrogen bond between pairs of ligands (see Fig. 2). Such H-bonds have also earlier been observed for Cu(II) compounds with ampym [1].

## Spectroscopy, EPR and Magnetism

The diffuse reflectance ligand field absorption of the title compound was observed as a set of several broad bands in agreement with the dark black-brown colour. A main maximum is found at $21.1 \cdot 10^3$ cm$^{-1}$ and a shoulder at $17.3 \cdot 10^3$ cm$^{-1}$, which are both assigned as charge transfer bands. The other band maxima at $12.5 \cdot 10^3$ and $10.0 \cdot 10^3$ cm$^{-1}$ are assigned to d–d transitions [26]. The lower CT energy, compared to the literature compound

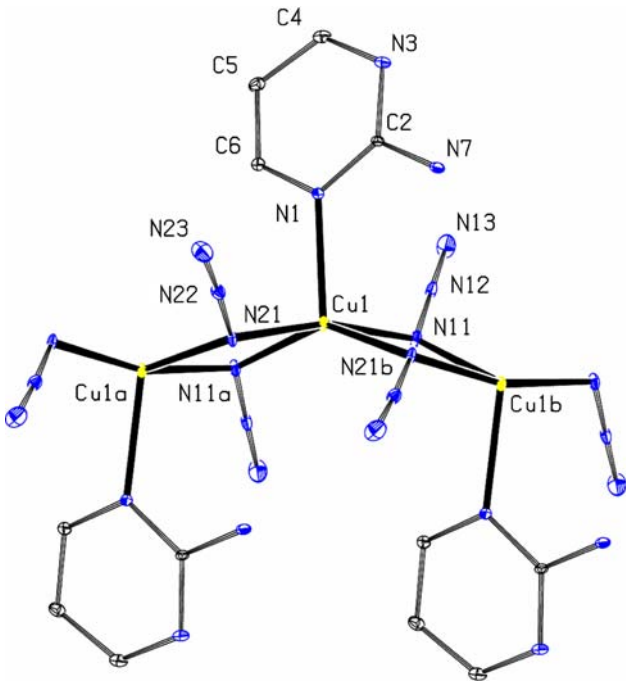


**Fig. 1** Atomic displacement plot (30% probability level) of the molecular structure of $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$. Hydrogen atoms are omitted for clarity

[20], is due to the fact that the title compounds has all short Cu–azide bands.

In the infrared spectrum, the characteristic azido infrared vibrations are observed at 2,062 ($\nu_{as}(N_3)$), 1,273 ($\nu_s(N_3)$) and 655 cm$^{-1}$ ($\delta(N_3)$). These values are consistent with those reported for other azido-bridged complexes [27–31].

In the far-infrared region two medium–strong absorptions assigned to the Cu–N($N_3$) and Cu–N($N_{Ligand}$) vibrations are observed at 370 and 224 cm$^{-1}$, consistent with those found in the literature [27–31].

The EPR spectrum of the title compound, measured from 50–600 mT as a polycrystalline powder shows, at RT, a very broad isotropic signal (peak-to-peak distance 245 mT) centred with a g-value of 2.03. At 77 K this signal sharpens up a little (peak-to-peak distance 175 mT) with $g = 2.05$. But even at 20 K the band is still broad (peak-to-peak distance 170 mT). Such broad signals are also observed in the literature for other azide-bridging Cu(II) compounds [31–33].

The magnetic susceptibility of a powdered sample was measured from 5 to 350 K. At 350 K the $X_MT$ value for one Cu(II) ion is 0.395 cm$^3$ K mol$^{-1}$, which is a little above the spin-only value for one non-interacting Cu(II) ion (0.375 cm$^3$ K mol$^{-1}$ at RT). This value stays constant till around 50 K when the $X_MT$ product value decreases gradually to a value of 0.150 cm$^3$ K mol$^{-1}$ at 5 K. This magnetic behaviour agrees with a weak antiferromagnetic exchange interaction [17].

**Table 2** Selected bond lengths (Å), hydrogen bonds and angles (°) for $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$

| | | | | |
|---|---|---|---|---|
| Cu(1)–N(11) | 1.998(3) | Cu(1)–N(21) | 2.001(3) | |
| Cu(1)–N(21)b | 2.034(3) | Cu(1)–N(11)a | 2.069(3) | |
| Cu(1)–N(1) | 2.169(3) | Cu(1)–Cu(1)a | 3.103(3) | |
| N(11)–Cu(1)–N(21) | 165.7(1) | N(21)a–Cu(1)–N(11)a | 143.9(1) | |
| N(11)–Cu(1)–N(1) | 94.9(1) | N(21)–Cu(1)–N(1) | 99.40(1) | |
| N(21)a–Cu(1)–N(1) | 111.4(1) | N(11)a–Cu(1)–N(1) | 104.70(1) | |
| Cu(1)–N(21)–Cu(1)b | 100.5(1) | | | |
| a = x, −y + 3/2, z + 1/2 | b = x, −y + 3/2, z − 1/2 | | | |
| *Hydrogen-bonding parameters* | | | | |
| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
| N(7)–H(7A)···N(21) [x, 3/2 − y, 1/2 + z] | 0.88 | 2.33 | 3.174(5) | 161 |
| N(7)–H(7B)···N(3) [1 − x, 1 − y, 2 − z] | 0.88 | 2.23 | 3.106(4) | 176 |

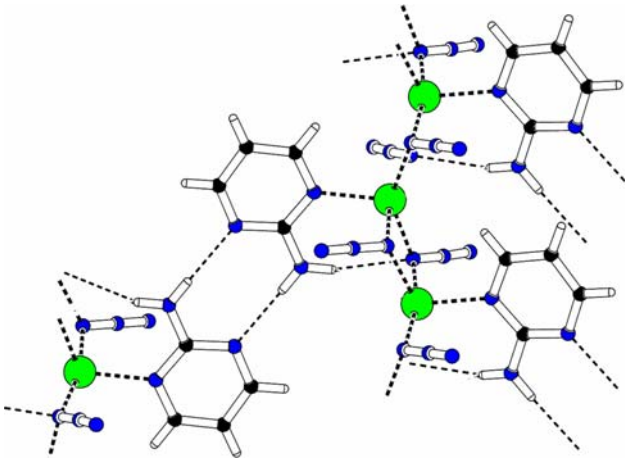

**Fig. 2** The hydrogen bond system between the chains of $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$ (see text)

## Conclusions

In this study a novel chain compound, $[Cu(ampym)(\mu_{1,1}\text{-}N_3)_2]_n$, has been synthesized and characterized by X-ray crystallography and spectroscopy. The coordination geometry around the Cu(II) ion is distorted square pyramidal. Two Cu(II) compounds in the literature exist with a similar type of structure, i.e. $[Cu(2\text{-chloropyrimidine})(\mu_{1,1}\text{-}N_3)_2]_n$ [20] and $[Cu(3,4\text{-lutidine})(\mu_{1,1}\text{-}N_3)_2]_n$ [21]. The main difference between these three compounds is the ligand. These last two ligands have no possibility to act as a hydrogen donor, with the result that no classical hydrogen bond exists in these two cases. In the title compound the amine group is the important hydrogen donor and form in this way a so-called Watson-Crick hydrogen bonding, whereas the second hydrogen bonding is observed between the amine group and the azide nitrogen. A weak antiferromagnetic interaction between the Cu(II) ions has been observed.

## Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-661738. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

**Acknowledgements** The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel MaterialenOnderzoek). Financial support and coordination by the FP6 Network of Excellence "MAGMA-Net"(contract number 515767) is kindly acknowledged.



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