Crystal structure, Hirshfeld surface analysis and physicochemical studies of two new Cu(II) complexes with the ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one

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Rim Boubakri^a, Christian Jelsch^b, Frédéric Lefebvre^c, Werner Kaminsky^d, Cherif Ben Nasr^a, Kamel Kaabi^{a,*}

^aLaboratoire de Chimie des Matériaux, Université de Carthage, Faculté des Sciences de Bizerte, 7021, Zarzouna, Tunisia

^bCRM2, CNRS, Institut Jean Barriol, Université de Lorraine, Vandœuvre les Nancy Cedex, France

^cLaboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, 69626 Villeurbanne Cedex, France.

^dDepartment of Chemistry, BOX 351700 University of Washington Seattle, WA 98195, USA.
Corresponding e-mail: kamel_kaabi@yahoo.fr

Abstract

The chemical preparation, crystal structure and spectroscopic characterization of two new Cu(II) complexes $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})_4](\text{CH}_3\text{COO})_2$, $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})$, **(1)** and $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})_2(\text{H}_2\text{O})_3](\text{CH}_3\text{COO})_2$, $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$, **(2)** with the monodentate ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one, (ampymo), are reported. In **(1)**, the Cu(II) atom is four-coordinated, in a square planar fashion, by nitrogen atoms of four ampymo ligands. In **(2)**, it is five-coordinated in a square pyramidal fashion by two pyrimidine nitrogen atoms and three water oxygen atoms. The crystal structure of **(1)** is stabilized by N–H···O hydrogen bonds with pillars of the cationic complexes alternating with channels occupied by the acetate anions. In the atomic arrangement of **(2)**, the complex cations are located parallel to the (a, b) plane between which the acetate anions intercalate by establishing hydrogen bonds with these cations to form a tridimensional network. The vibrational absorption bands were identified by infrared spectroscopy. Intermolecular interactions were investigated via Hirshfeld surfaces and electronic properties such as HOMO and LUMO energies were derived.

Keywords: Square planar; Square pyramidal; Cu(II) complex; X-ray diffraction; Coordination compound; Hirshfeld surface.

1. Introduction

The rational design and synthesis of transition metal complexes have become very attractive research fields owing to their intriguing structural diversity and enormous potential applications such as gas storage [1], gas separation [2], ion-exchange [3], molecular electronics [4], luminescence [5], non-linear optical behavior [6] and magnetism [7]. These complexes have also drawn increased attention because of their important role in the field of bio-inorganic chemistry. Among them, copper complexes have been extensively studied because of their widespread use in a range of applications ranging from catalysis [8] to medicinal chemistry [9, 10] or electro-optics [11, 12]. The properties of complexes are dependent on the nature of coordinating ligands and donor atoms. Copper complexes containing heterocyclic organic ligands, such as pyrimidine, have shown a wide range of biological and pharmaceutical activities that include DNA binding and cleavage, antimicrobial, anticancer and antioxidant behavior [13 -16]. Pyrimidine ring systems in nucleic acids, vitamins and coenzymes offer some effective binding sites for metal ions. The presence of more than one hetero-atom and the higher π acidity of the pyrimidine ring as compared to that of pyridine bases play an important role in coordination chemistry and also serve to improve biological systems [17-19].

As part of our continuous involvement in the study of metal complexes of ligands of interesting molecular structures for suitable applications [20], we report here the synthesis and structural characterization of two Cu(II) complexes with the ampymo (2-amino-6-methylpyrimidin-4-(1*H*)-one) ligand (Scheme 1). This work indicates that the solvent used in the synthesis of the compounds has a direct effect on the crystal structure diversity. Indeed, by

use of the same reagents in the synthesis but of two different solvents, two crystal structures with a different unit cell content were obtained.

Scheme 1. Structural formula of ampymo (2-amino-6-methylpyrimidin-4-(1*H*)-one).

2. Experimental

2. 1. Chemical preparation

2.1.1. Preparation of $[Cu(ampymo)_4](O_2CMe)_2$ (**1**)

A solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (10 mg, 0.025 mmol) in ethanol (10 mL) was added dropwise to a solution of ampymo (26 mg, 0.2 mmol) in ethanol (10 mL). After stirring for 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after five days by evaporating the filtrate at room temperature (yield = 71%). Anal. Calc.: C, 42.21; H, 4.98; N, 24.62%. Found: C, 41.92; H, 4.56; N, 24.43 %.

2.1.2. Preparation of $[Cu(ampymo)_2(H_2O)_3](O_2CMe)_2$ (**2**)

A solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (10 mg, 0.025 mmol) in water (10 mL) was added dropwise to a solution of ampymo (13 mg, 0.1 mmol) in water (20 mL). After stirring for 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after five days by evaporating the filtrate at room temperature (yield = 67%). Anal. Calc.: C, 34.60; H, 5.35; N, 17.29%. Found: C, 34.12; H, 5.72; N, 17.06 %.

2. 2. X-ray single crystal structural analysis

2. 2.1. X-ray single crystal structural analysis of (**1**)

A colorless prism, measuring 0.33 x 0.11 x 0.10 mm³ was mounted on a loop with oil. Data were collected at 100 K on a Bruker APEX II single crystal X-ray diffractometer using Mo-radiation. The crystal-to-detector distance was 40 mm and the exposure time was 10 seconds per frame for all sets. The scan width was 0.5°. Pertinent experimental details are listed in Table S1. The diffraction data were integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker [21]. Solution by direct methods (SHELXS, SIR97 [22]) produced a complete heavy atom phasing model consistent with the proposed structures. The structures were completed by difference Fourier synthesis with SHELXL [23, 24]. Scattering factors are from Waasmair and Kirfel [25]. Isotropic thermal parameters U_{eq} of hydrogen atoms were fixed such that they were 1.2 U_{eq} of their parent atom U_{eq} for CH's, NH's, and NH₂'s - and 1.5 U_{eq} in the case of methyl groups. NH and NH₂ groups were refined with fixed NH and H···H distance restraints so that the NH₂ groups were free to rotate and tilt with respect to the C-N bonds. Bond length restraints were set in accord with following table:

	methane	methyl	N-H	N-H ₂	H···H (NH ₂)
d(X-H) (Å)	0.95	0.98	0.86	0.86	1.49

All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. The drawings were made with Diamond [26] and Mercury [27].

2.2.2. X-ray single crystal structural analysis of (**2**)

Intensity data for (**2**) were collected at 293 K on a New Xcalibur, EosS2 single crystal diffractometer using graphite monochromated Mo-K α radiation ($k = 0.71073$ Å). Unit cell determination, data collection and data reduction were performed using the CrysAlisPro software [28]. A symmetry-related (multiscan) absorption correction had been applied. The structures were solved with SHELXT [29] and refined by a full-matrix least-squares procedure based on F^2 (Shelxl-2014) [23]. Four square aligned residual electron density maxima of up to 1.12 eÅ³ were found, located co-planarly with the ligands at about 1 Å distance from the copper

atom. The crystal data are gathered in Table S1. The drawings were made with Diamond [26] and Mercury [27].

2.3 IR spectroscopy

The spectra were recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer FTIR spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

2.4. DFT calculations

Quantum chemical calculations were performed with the Gaussian 09 program on the two copper complexes. As periodic calculations should be too time-consuming and in order to describe the complex in the solid state, these calculations were done on the geometry determined by X-ray crystallography. However, as the C-H, O-H and N-H distances were too short compared to what is usually observed in theoretical calculations (by X-ray crystallography they were assumed to be in a 0.95 – 1.00 Å range, see above, while theoretical calculations give 1.05 to 1.09 Å), an optimization of the proton positions was done first. The HOMO and LUMO and the Mulliken charge distribution were then determined of these semi-optimized geometries. In the two cases the theoretical infrared spectrum was obtained by summing the individual spectra of two acetate ions and the cationic copper complex. All calculations were done with the classical B3LYP method and the 6-31+G* basis set for all atoms.

2.5 Hirshfeld surface analyses.

Fingerprint plots were obtained with the CrystalExplorer program [30]. The contact types and their enrichment were analyzed with the program MoProViewer [31]. Moieties in the crystal packing not in contact with each other were selected in order to obtain an integral Hirshfeld surface around each molecule/ion. For compound (**1**), the Hirshfeld surface was computed for two copies of the asymmetric unit as the Cu atom lies on a special position and

has a multiplicity of 2. For electrostatic energy calculations, the electron density of the molecules was modeled by transfer from the ELMAM2 multipolar atoms database [32]. In both compounds, the copper cation was set spherical with a charge of +2e while the asymmetric unit was set electrically neutral.

3. Results and Discussion

3.1. X-ray diffraction study

3.1.1. Structure description of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})$ (**1**)

The main geometrical features of the different chemical entities of $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})_4](\text{CH}_3\text{COO})_2$ are reported in Tables 1 and S2. X-ray crystal structure analysis reveals that $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})$ crystallizes in the monoclinic space group $P4_2/n$. The asymmetric unit consists of one Cu(II) cation, two ampymo ligands and one acetate anion (Fig. 1). In the atomic arrangement of this complex, the Cu(II) atom is coordinated in a square planar fashion by four nitrogen atoms N1, N1ⁱ, N4 and N4ⁱ ($i = 1-x+3/2, -y+1/2, z$), each belonging to a different ampymo ligand molecule. Distances are equal with Cu–N1 = 2.0234(12) and Cu–N4 = 2.0257(12) Å. The sum of the angles around the Cu atom (N1–Cu–N1ⁱ = 90.89 (7), N1–Cu–N4ⁱ = 90.23(5), N1ⁱ–Cu–N4ⁱ = 90.23(5), N4–Cu–N4ⁱ = 88.89 (7)°) is close to 360° showing that the N1, N1ⁱ, N4, N4ⁱ and Cu(II) atoms are coplanar. An additional non-bonding copper environment is set up from the four keto oxygen atoms with Cu···O distances of 2.786(4) to 2.807(6) Å. The potentially bidentate ligand ampymo is acting only in a mono-dentate fashion. In the atomic arrangement, the complex cations are arranged in periodic pillars of individual complexes that interact with their neighbors in the *c*-axis direction. The pillars are alternated with channels filled with the acetate anions (Fig. 2) that play a role of linking the neighboring complex cations through N2–H···O3 and N5–H···O4 hydrogen bonds (see Table 1) to form a 1-D corrugated chain running along the *b*-axis direction (Fig. 3). The donor acceptor distances N2···O3, N6···O3 and N5···O4 of these hydrogen bonds are 2.767(2), 2.920(2) and 2.782(2)

Å, respectively. The crystal packing is also stabilized by intramolecular hydrogen bonds N6–H···O1, N3–H···O1, N3–H···O2, N6–H···O2 and by weak C–H.... π intermolecular interactions between hydrogen atoms of the acetate methyl group and the neighboring aromatic ring with an H··· π distance of 4.004 Å [33–35] (Fig. S1). Geometrical details of the organic part, summarized in Table S2, show the C–N bond lengths of the NH₂ groups of N3–C1 [1.323 (3) Å] and N6–C6 [1.328 (3) Å] to be approximately equal to that of a C=N double bond. Similar bond lengths were previously observed for the imine form due to amine-imine tautomerism of organic cations [36, 37]. The C2–O1 [1.250 (3) Å] and C7–O2 [1.253 (3) Å] distances are typical for ketonic oxygen [36, 37]. In both cases, the tautomerism increases compound stability.

3.1.2. Structure description of $[Cu(ampymo)_2(H_2O)_3](O_2CMe)_2$ (**2**)

The main geometrical features of the different chemical entities of complex (**2**) are given in Tables 2 and S3. The X-ray diffraction study of a single crystal of (**2**) shows that this compound crystallizes in the space group $P2_1/n$. The asymmetric unit consists of one Cu(II) cation, two ampymo ligands, three coordinated water molecules and two acetate anions (Fig. 4). The copper atom Cu(II) is penta-coordinated in a square pyramidal fashion by two pyrimidine nitrogen atoms (N1 and N4) as well as two water oxygen atoms (O3 and O4) in basal positions and one water oxygen atom O5 at the apex. The Cu–N bond lengths (Cu–N1 = 2.004(4) and Cu–N4 = 2.017(4) Å) are close to those reported for other complexes [36, 37]. The apical Cu–O bond length (Cu–O5 = 2.463(4) Å) is larger than the basal Cu–O ones (Cu–O3 = 1.969(3), Cu–O4 = 1.966(3) Å). This fact may be ascribed to a Jahn-Teller distortion. These bond lengths are comparable to corresponding values in similar coordination compounds [38, 39]. The sum of the basal bond angles around the Cu atom (N1–Cu–O3 = 92.42(14), O3–Cu–N4 = 89.46(14), N4–Cu–O4 = 90.99(14), O4–Cu–N1 = 88.13(14)°) is close to 360°, showing that the basal atoms (N1, N4, O3 and O4) are coplanar. The N1–Cu–N5 angle [100.59 (17)°] for

the CuN₂O₃ coordination polyhedron shows a significant deviation from the ideal value of 90°. Similarly, N3-Cu-N1 angle amounts to 163.8(1)°, which is far from the ideal value 180°. These geometrical parameters indicate that the CuN₂O₃ entity has a distorted pyramidal geometry (Fig. 4). In the atomic arrangement, the cationic complexes [Cu(ampymo)₂(H₂O)₃]²⁺ are located parallel to the (**a**, **b**) planes at $z = \frac{1}{2}n$ (Fig. 5), between which the acetate anions intercalate and connect them through hydrogen bonds to form a tridimensional network (Fig. 5 and Table 2). These H-bonds are of the N–H···O and O–H···O type in which the imine nitrogen atoms and the oxygen atoms of the coordinated water molecules play a role as donors and the oxygen atoms of the acetate anions play a role as acceptors. The distances N···O and O···O are in the [2.682 (5) - 2.935 (6) Å] and [2.678 - 2.712 Å] ranges, respectively. Fig. 6 represents the projection along c-axis at $z = 0$ (the acetate anions are omitted for clarity) and shows that the water oxygen atom O5 at the apex and the oxygen atom O2 of the organic ligand of neighboring complex molecules are linked through four O–H···O hydrogen bonds forming a cyclic hydrogen-bonded with graph-set motif $R_2^2(8)$. The donor···acceptor distances O5···O2 of these hydrogen bonds are 2.638 and 2.771 Å. The crystal packing is also stabilized by intramolecular hydrogen bonds N3–H···O5 and N6–H···O1. The bond lengths and the angles in the organic molecules of (**2**) are similar to those of the organic molecules in (**1**), showing that the organic molecules in the two compounds have the same characteristics.

It is worth to note that 3d-metal complexes of the same ligand with different nuclearities and coordination modes were previously described in the literature [36, 37, 40-42] (Table S4).

3.2. Hirshfeld surface analysis

3.2.1. Contacts of (**1**)

The Hirshfeld surface is representative of the region in crystalline space where molecules come into contact allowing the analysis of the chemical nature of intermolecular interactions. Table 3 shows the proportions C_{xy} of the different contact types. The contact

enrichment ratio E_{xy} is obtained by comparing the actual contacts C_{xy} with those computed as if all contacts had the same probability to form. An enrichment ratio larger than unity indicates that the contact type is favored and over-represented in the crystal [43].

The hydrophobic atoms C and Hc constitute 56% of the Hirshfeld surface and Hc...Hc contacts have the highest proportion at 17.7% (Table 3a). Globally hydrophobic contacts involving C and Hc represent 38% of the surface. The pyrimidine aromatic cycle does not display any parallel stacking; the C...C contacts are, however, enriched as four pyrimidines tend to form tetrahedral cages (Fig. 7-a). C-H... π weak H-bonds are slightly under-represented ($E=0.92$) and occur mainly between the methyl group of acetic acid and the pyrimidine heterocycle. The cross contacts between hydrophobic (C, Hc) atoms and charged atoms are all disfavored, as atoms from each subset prefer to interact within their own group.

The N...Cu coordination bonds represent less than 6% of the contact surface but are, by far, the most enriched at $E=7.0$. The central short spikes in the fingerprint plots originate from the N...Cu interactions. Comparatively the O...Cu contacts ($d > 2.67 \text{ \AA}$) are at longer distances than the N...Cu ones (Table S2); they are much less abundant and only very slightly enriched. The Hirshfeld surface around the Cu(II) cation has a square shape in the CuN₄ plane and is bifacial and elongated in the orthogonal direction (Fig. 7-b).

The strong O...Hn hydrogen bonds constitute the second largest interaction surface and have the second largest enrichment ($E=3.0$), while the weak O...Hc hydrogen bonds are the fourth interaction in proportion and are slightly under-represented.

3.2.2. Contacts of (2)

The chemical content of crystal (2) indicates a higher proportion of oxygen and polar hydrogen Hn/o atoms compared to compound (1), due to the hydration of the crystal by three water molecules (Table 3b). As a result, only 45% of the surface involves the C and Hc atom types. The contacts between these hydrophobic atoms are slightly over-represented ($E=1.22$), as they

amount to 37% of the interactions. All the cycles in the crystal are close to be coplanar which results in a high degree of cycle stacking, the C $\cdots$ C and C $\cdots$ N contacts are particularly enriched while N $\cdots$ N is well represented. The contact in **(2)** with largest surface is constituted by the quite over-represented strong hydrogen bonds O $\cdots$ Hn.

The copper cation is more in contact with oxygen atoms, but the Cu $\cdots$ N contact is still the most enriched one at $E_{\text{CuN}} = 4.37$. The Cu(II) Hirshfeld surface has nearly a cuboid shape, except that the face without ligand is convex (Fig. 7c).

3.2.3. *Electrostatics of contacts*

The scatterplot of the average electrostatic energy E_{elec} as a function of enrichment values is shown in Fig. 8-a,b for the different contact types. The graphs confirm that the two crystal packings are maintained primarily by three types of strongly attractive interactions with high enrichment, namely the coordination interactions Cu–N and Cu–O, followed by the O $\cdots$ Hn strong hydrogen bonds.

In both compounds, self-interactions between charged species (Cu $^{2+}$, N $^{\delta-}$, O $^{\delta-}$, Hn $^{\delta+}$) which are repulsive are mostly avoided, except for N $\cdots$ N, due to the stacking of the heterocycles. The very unfavorable Cu $\cdots$ Hn contact in compound **(2)** is due to proximity effects with the Cu $\cdots$ O coordination with water. The Hc $\cdots$ Hc and C $\cdots$ C contacts have low electrostatic energy but appear enriched due to the hydrophobic effect. Globally the two compounds show similar features in Fig. 8.

3.3. *Quantum mechanical studies*

3.3.1. *Quantum mechanical study of compound **(1)***

Quantum chemical calculations were performed from the crystal data with the DFT method at the 6-31+G* basis set, by using the Gaussian 09 software package [44]. The energies of the frontier orbitals of the compound **(1)** are listed in Table 4. Fig. 9 clearly shows that the highest occupied orbital (HOMO) is located on one of the two crystallographic independent organic

ligands, specifically on the C4 carbon atom bearing a methyl group and on the adjacent C3 carbon, while the lowest unoccupied orbital (LUMO) is mainly located on the other organic ligand. The large HOMO-LUMO gap of 5.53 eV implies high kinetic stability and low chemical reactivity [45, 46].

The Molecular Electrostatic Potential (MEP) surface is depicted on Fig. S2. Blue and red colors indicate the positive and negative potentials, respectively. As it can be seen, the electrostatic potential maps are color-coded and are subdivided into many regions where those various colors are used to identify different potentials. Intermediate potentials are assigned to colors according to the following color spectrum: red < orange < yellow < green < blue. and confirms the above results with the most negative part near copper and the surrounding with positive charges.

3.3.2. *Quantum mechanical study of compound of (2)*

The HOMO and LUMO orbitals were determined for the cationic complex and the two acetate groups interacting with it, in order to describe the hydrogen bonds between the CH_3COO^- groups of acetate and the N–H bonds of the organic ligands. Although it is difficult to determine discrete orbitals for a crystal (a better choice would be to perform periodic calculations which are highly time consuming) a good approximation of the gap between the occupied and unoccupied bands can be obtained by this way. The energies of the frontier orbitals of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$ are listed in Table 4. Fig. 10 shows the HOMOs and LUMOs and the next orbitals for the title compound calculated at the B3LYP/6-31++G**.

Clearly the highest occupied orbitals are localized mainly on the acetate groups, while the lowest unoccupied orbitals are mainly on the two organic ligands around the copper. The gap between the LUMO and the HOMO is 4.13 eV. As for (1), this large energy gap characterizes a high chemical hardness and kinetic stability of the new coordination compound.

The molecular electrostatic potential of the title compound has been computed at the B3LYP/6-31++G** level and is shown in Fig. S3. As seen from this figure, the negative zones are mainly on the acetate groups, the positive zones being at the proton level of the N–H bonds.

3.4. IR spectroscopy

The IR absorption spectra of two compounds **(1)** and **(2)** are shown in Figs. S4-a and S5-a. The two spectra are similar and the most representative and characteristic vibrational modes of these compounds can be compared to those of similar compounds [47–49]. The bands in the high wavenumber region on the two spectra, between 3500 and 2800 cm⁻¹, correspond to the stretching vibrations of the NH and CH groups for **(1)** and to the stretching vibrations of the NH, CH and OH groups for **(2)**. These groups are interconnected by a system of hydrogen bonds in the crystal [50]. Bands in the 1700 - 1400 cm⁻¹ region of the two spectra correspond to the stretching vibrations of the acetate (OCO) groups and of the C=C, C=N and C=O groups of the organic ligands and to the N–H, C–H and O–H bending vibrations [51]. The bands in the range 1300 - 1000 cm⁻¹ can be attributed to the valence vibrations of the C–C, C–N and acetate C–O groups. Bands in the 1000 - 500 cm⁻¹ region correspond to the out of plane bending modes of C–H, N–H, C–C and C–N groups and to deformation mode of acetate (OCO) group [52, 53].

The calculated IR spectra are given in Figs. S4-b and S5-b. There is a good agreement between the experimental and calculated spectra even if the intensities are not similar but this is related to the line width, which is greater for some experimental lines due to the hydrogen bonds (see for example the bands at ca. 1580 and 1407 cm⁻¹ in the two spectra). There is almost no difference between the experimental and calculated spectra after optimization of the protons positions. The correlation is good ($R = 0.9974$ for the spectrum of compound **(1)**, $R = 0.9989$ for the spectrum of compound **(2)**), as shown in the correlation plot, Fig. S6, but some bands were omitted for which the calculated intensity is too low. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

4. Conclusion

Two new Cu(II) complexes, $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$ and $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$, were synthesized as single crystals at room temperature and characterized by various physico-chemical methods. According to the X-ray structural results, the different components are held together in the packing arrangement by means of several $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds forming three-dimensional networks. The enrichment ratio, derived from the Hirshfeld contact surface analysis, allows determining which types of contacts are over- or under-represented in the two crystal packings. The coordination $\text{Cu}-\text{N}$ and $\text{Cu}-\text{O}$ interactions are the most attractive from an electrostatic energy point of view and are both quite enriched in the two compounds. Along with the strong and over-represented $\text{O}\cdots\text{H}/\text{n}$ hydrogen bonds, these interactions can be identified as the driving force in the packing formation. The hydrophobic atoms (Hc and C) tend to interact within their subgroup, with a very small electrostatic energy. In both compounds, $\text{C}\cdots\text{C}$ interactions are quite over-represented, due to non-parallel and parallel stacking in compound **(1)** and **(2)** respectively. DFT calculations allow the attribution of the experimental IR bands at low frequencies. Further studies of biological evaluation and magnetic properties of these Cu(II) complexes are in progress.

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1877359 for **(1)** and CCDC No 1939573 for **(2)**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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Figure captions

Fig. 1. ORTEP of the structure of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$ with displacement ellipsoids drawn at the 50% probability level (i:1 $-x+3/2, -y+1/2, z$). Dotted lines indicate hydrogen bonds.

Fig. 2. Projection of the structure of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$ along the c -axis.

Fig. 3. View of the 1D chain $\{[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2\}_n$ along c -axis.

Fig. 4 ORTEP of the structure of the $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$ compound with displacement ellipsoids drawn at the 50% probability level. Dotted lines indicate hydrogen bonds.

Fig. 5 Projection of the structure of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$ along the a -axis.

Fig. 6 Projection of the structure of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$ along the c -axis. Acetates ions are removed for clarity of the figure. Dotted lines indicate hydrogen bonds.

Fig. 7 (a) View of four pyridine groups forming a tetrahedral cage. (b) View of the Hirshfeld surface around the Cu(II) cation in compound (1) and (c) in compound (2). The surface is colored according to the interacting atom: blue: nitrogen, red: oxygen, white: Hn/o nitrogen.

Fig. 8 Scatterplot of average electrostatic energy $\langle E_{\text{elec}} \rangle$ as a function of enrichment for the different contact types. (repulsive Cu.Cu with no contact ($E=0$) is not represented). (a) in compound (1), (b) in compound (2). Hp represents the polar hydrogen atoms Ho/n bound to oxygen or nitrogen.

Fig. 9 Frontier orbitals in $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$.

Fig. 10 Frontier orbitals in $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$.

Fig. 1

Fig. 2

Fig. 3

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Table 1 [Hydrogen-bond geometry \(Å, °\)](#) in complex (**1**).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2···O3	0.86	1.91	2.767 (2)	172 (2)
N3—H3 <i>A</i> ···O1 ⁱ	0.86	2.23	3.000 (2)	149 (2)
N3—H3 <i>A</i> ···O2 ⁱ	0.86	2.41	2.952 (2)	122 (1)
N3—H3 <i>B</i> ···O4	0.86	2.05	2.898 (2)	168 (2)
N5—H5···O4 ⁱⁱ	0.86	1.93	2.782 (2)	172 (2)
N6—H6 <i>A</i> ···O2 ⁱ	0.86	2.24	2.971 (2)	144 (2)
N6—H6 <i>A</i> ···O1 ⁱ	0.86	2.42	3.035 (2)	129 (1)
N6—H6 <i>B</i> ···O3 ⁱⁱ	0.86	2.06	2.920 (2)	176 (2)

Symmetry codes: (i) $-x+3/2, -y+1/2, z$; (ii) $y+1/2, -x+1, z-1/2$.

Table 2 [Hydrogen-bond geometry](#) (Å, °) in complex **(2)**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2···O8	0.86	1.90	2.752 (5)	172
N5—H4 <i>A</i> ···O6	0.86	1.83	2.682 (5)	171
N5—H4 <i>A</i> ···O7	0.86	2.86	3.541 (5)	137
N3—H3 <i>A</i> ···O5	0.86	1.90	2.732 (6)	161
N3—H3 <i>B</i> ···O9	0.86	1.97	2.820 (6)	169
N6—H6 <i>A</i> ···O1	0.86	2.15	3.011 (5)	174
N6—H6 <i>B</i> ···O7	0.86	2.10	2.953 (6)	170
O5—H5 <i>O</i> ···O2	0.80	1.90	2.639 (6)	153
O3—H3 <i>O</i> ···O8 ⁱ	0.80	1.88	2.680 (5)	174
C14—H14 <i>A</i> ···O1 ⁱ	0.96	2.66	3.382 (8)	132
O4—H4 <i>P</i> ···O6 ⁱⁱ	0.80	1.89	2.677 (6)	171
C12—H12 <i>A</i> ···O2 ⁱⁱ	0.96	2.56	3.312 (6)	135
O3—H3 <i>P</i> ···O9 ⁱⁱⁱ	0.80	1.96	2.713 (8)	157
O4—H4 <i>O</i> ···O7 ^{iv}	0.80	1.91	2.699 (5)	169
O5—H5 <i>P</i> ···O2	0.80	1.98	2.772 (5)	171

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x-1/2, -y+1/2, z-1/2$.

Table 3. Statistical analysis of intermolecular contacts on the Hirshfeld surface of compounds **(1)** and **(2)**. The second row shows the chemical content on the Hirshfeld surface. The middle part shows the proportions C_{xy} of the different contact types and the lower part shows the E_{xy} enrichment ratios of contact types. Reciprocal contact type X...Y and Y...X are merged. The main contacts and the most enriched ones are highlighted in bold. The hydrophobic (C, Hc) atoms and charged (Cu, N, O, Hn) atoms have been regrouped in the Table.

(a)

atom	Cu	N	O	Hn	Hc	C
Surface %	3.5	8.6	16.9	15.2	35.5	20.4
Cu	0.0				contacts	%
N	5.9	1.1				
O	2.1	0.8	0.2			
Hn	1.0	0.8	15.8	1.2		
Hc	0.1	3.5	11.3	7.9	17.7	
C	1.5	2.2	3.7	2.8	12.5	8.0
Cu	0.00				enrichment	
N	7.00	1.84				
O	1.18	0.31	0.08			
Hn	0.59	0.35	3.00	0.49		
Hc	0.02	0.64	0.93	0.73	1.42	
C	0.73	0.74	0.56	0.48	0.92	2.13

(b)

atom	Cu	N	O	Hn/o	Hc	C
surface %	5.4	5.9	22.1	22.6	28.8	15.2
Cu	0.0				contacts	%
N	4.2	0.3				
O	8.3	1.0	0.0			
Hn/o	2.9	1.2	21.4	1.1		
Hc	1.3	0.8	8.3	12.6	12.7	
C	0.8	2.7	4.2	4.1	7.0	5.1
Cu	0				enrichment	
N	4.37	1.06				
O	2.18	0.45	0.01			
H	0.73	0.51	2.23	0.23		
Hc	0.27	0.28	0.69	1.03	1.65	
C	0.32	1.79	0.67	0.63	0.87	2.44

Table 4. Energy values of frontier orbitals in compounds **(1)** and **(2)**

	Compound (1)		Compound (2)	
Orbitals	Spin	Energy (eV)	Spin	Energy (eV)
HOMO-3	Beta	-11.898	Alpha	-6.018
HOMO-2	Alpha	-11.896	Alpha	-6.015
HOMO-1	Beta	-11.777	Beta	-6.013
HOMO	Alpha	-11.776	Beta	-5.991
LUMO	Alpha	-6.239	Alpha	-1.858
LUMO+1	Alpha	-6.181	Alpha	-1.690
LUMO+2	Alpha	-6.154	Alpha	-1.632
LUMO+3	Alpha + Beta	-6.079	Alpha	-1.2362

Supplementary Information

Crystal Structure, Hirshfeld surface analysis and physicochemical studies of two new Cu(II) complexes with the 2-amino-6-methylpyrimidin-4-(1H)- one ligand

Rim Boubakri^a, Christian Jelsch^b, Frédéric Lefebvre^c, Werner Kaminsky^d, Cherif Ben Nasr^a,
Kamel Kaabi^{a,*}

^aLaboratoire de Chimie des Matériaux, Université de Carthage, Faculté des Sciences de Bizerte,
7021, Zarzouna, Tunisia

^bCRM2, CNRS, Institut Jean Barriol, Université de Lorraine, Vandœuvre les Nancy Cedex,
France

^cLaboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie
Physique Electronique, 69626 Villeurbanne Cedex, France.

^dDepartment of Chemistry, BOX 351700 University of Washington Seattle, WA 98195, USA.
Corresponding e-mail: kamel_kaabi@yahoo.fr

Fig. S1 Intermolecular interactions C-H... π between hydrogen atoms of methyl group –CH₃ and the neighboring aromatic rings in [Cu(ampymo)₄](O₂CMe)₂.

Fig. S2 MEP surface of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$.

Fig. S3 MEP surface of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$.

Fig. S4 (a) Experimental Infrared absorption spectrum. (b) Calculated infrared absorption spectrum of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$.

Fig. S5 (a) Experimental Infrared absorption spectrum. (b) Calculated infrared absorption spectrum of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$

Fig. S6 Comparison between experimental and calculated IR frequencies (a) of $[\text{Cu}(\text{ampymo})_4](\text{O}_2\text{CMe})_2$, (b) of $[\text{Cu}(\text{ampymo})_2(\text{H}_2\text{O})_3](\text{O}_2\text{CMe})_2$

Table S1: Experimental details of compounds **(1)** and **(2)**

Compounds	Compound (1)	Compound (2)
Empirical formula	C ₂₄ H ₃₄ Cu N ₁₂ O ₈	C ₁₄ H ₂₆ Cu N ₆ O ₉
Formula weight	682.17	485.95
Temperature	100(2) K	293 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Monoclinic
Space group	P 4 ₂ /n	P2 ₁ /n
Unit cell dimensions	<i>a</i> = 14.2120(10) Å <i>b</i> = 14.2120(10) Å <i>c</i> = 16.6729(14) Å	<i>a</i> = 12.1887 (10) Å <i>b</i> = 12.3732 (8) Å <i>c</i> = 14.2797 (8) Å, β = 98.751 (6)°
Volume (Å ³)	3367.6(4)	2128.5 (3)
<i>Z</i>	4	4
Density (calculated) (Mg/m ³)	1.345	1.516
Absorption coefficient (mm ⁻¹)	0.709	1.08
<i>F</i> (000)	1420	1012
Crystal size	0.33 x 0.11 x 0.10 mm ³	0.32 × 0.21 × 0.19
Diffractometer	Bruker APEX II	New Xcalibur, EosS2
Theta range for data collection	1.88 to 28.35°.	3.4 to 28.2°
Index ranges	-18 ≤ <i>h</i> ≤ 18, -18 ≤ <i>k</i> ≤ 18, -22 ≤ <i>l</i> ≤ 22	-10 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 16
Reflections collected	116312	8541
Independent reflections	4189 [<i>R</i> (int) = 0.0382]	3884 [<i>R</i> (int) = 0.049]
No. of reflections	4189	3884
No. of parameters	225	293
No. of restraints	8	9
Goodness-of-fit on <i>F</i> ²	1.033	1.06
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0329, <i>wR</i> 2 = 0.0776	<i>R</i> 1 = 0.077, <i>wR</i> 2 = 0.219,
Largest diff. peak and hole	0.309 and -0.553 e.Å ⁻³	1.44 and -1.46 e.Å ³

Table S2. Selected bond distances and angles (Å, °) in complex **(1)**.

Cu1-N1	2.023(1)	C3-C4	1.352(2)	C7-N4	1.384(2)
Cu1-N4	2.026(1)	C4-N2	1.377(2)	C7-C8	1.439(2)
C1-N3	1.323(2)	C4-C5	1.497(2)	C8-C9	1.344(2)
C1-N1	1.338(2)	C6-N6	1.328(2)	C9-N5	1.380(2)
C1-N2	1.362(2)	C6-N4	1.339(2)	C9-C10	1.498(2)
C2-O1	1.250(2)	C6-N5	1.358(2)	C11-O3	1.260(2)
C2-N1	1.386(2)	C7-O2	1.253(2)	C11-O4	1.274(2)
C2-C3	1.438(2)			C11-C12	1.507(2)
N1 ⁱ -Cu1-N1	90.89(7)	C4-C3-C2	119.64(14)	C8-C9-N5	119.22(14)
N1 ⁱ -Cu1-N4	90.23(5)	C3-C4-N2	119.23(13)	C8-C9-C10	124.87(15)
N1-Cu1-N4	176.14(5)	C3-C4-C5	125.18(14)	N5-C9-C10	115.91(15)
N4-Cu1-N4 ⁱ	88.89(7)	N2-C4-C5	115.59(13)	O3-C11-O4	122.87(15)
N3-C1-N1	120.96(13)	N6-C6-N4	120.70(13)	O3-C11-C12	118.63(14)
N3-C1-N2	118.37(13)	N6-C6-N5	118.61(15)	O4-C11-C12	118.47(14)
N1-C1-N2	120.67(14)	N4-C6-N5	120.69(14)	C1-N1-C2	120.54(12)
O1-C2-N1	117.21(13)	O2-C7-N4	117.22(13)	C1-N2-C4	121.55(13)
O1-C2-C3	124.48(14)	O2-C7-C8	124.42(15)	C6-N4-C7	120.37(13)
N1-C2-C3	118.31(13)	N4-C7-C8	118.36(15)	C6-N5-C9	121.54(14)
		C9-C8-C7	119.76(15)		

Symmetry code: (i) $-x+3/2, -y+1/2, z$ **Table S3.** Selected bond distances and angles (Å, °) in complex **(2)**.

N1—Cu1	2.004 (3)	O4—Cu1—O3	176.43 (15)
N4—Cu1	2.018 (3)	O4—Cu1—N1	88.13 (14)
O3—Cu1	1.969 (3)	O3—Cu1—N1	92.42 (14)
O4—Cu1	1.966 (3)	O4—Cu1—N4	90.99 (14)
O5—Cu1	2.463(4) Å	O3—Cu1—N4	89.46 (14)
		N1—Cu1—N4	163.80 (15)

Table S4. Nuclearities and coordination modes of 3d-metal complexes with ampymo ligand.

Compounds	nuclearity	coordination mode	
		Metal (1)	Metal (2)
[Cd(NO ₃) ₂ (ampymo) ₂] [40]	mononuclear	eight-coordinated	-
[CdCl ₂ (ampymo) ₂] [41]	mononuclear	hexacoordinated	-
[Cu(ampymo) ₄]SO ₄ ·4H ₂ O [42]	mononuclear	tetracoordinated	-
[Cu(ampymo) ₄]Cl ₂ ·5H ₂ O [36]	mononuclear	tetracoordinated	-
[Cu(ampymo) ₄][Cu(H ₂ O) ₅](ClO ₄) ₄ ·6H ₂ O [37]	binuclear	tetracoordinated	pentacoordinated
[Cu ₂ (ampymo) ₄ (H ₂ O) ₃](ClO ₄) ₄ ·½H ₂ O [37]	binuclear	tetracoordinated	hexacoordinated
[Ni(ampymo) ₄][Ni(H ₂ O) ₆](ClO ₄) ₄ ·5H ₂ O [37]	binuclear	tetracoordinated	pentacoordinated

```

data_nasr_1_0m

_audit_creation_date      2016-04-05T12:00:50-00:00
_audit_creation_method    'WinGX routine CIF_UPDATE'
_audit_conform_dict_name  cif_core.dic
_audit_conform_dict_version 2.4
_audit_conform_dict_location
ftp://ftp.iucr.org/pub/cif_core.dic
_publ_requested_category  FM

#-----#
#
#          CHEMICAL INFORMATION
#
#-----#

_chemical_name_systematic
;
nasr_1
;
_chemical_name_common      nasr_1
_chemical_formula_moiety    'C20 H28 Cu N12 O4, 2(C2 H3
O2)'
_chemical_formula_sum      'C24 H34 Cu N12 O8'
_chemical_formula_weight    682.17

#-----#
#
#          UNIT CELL INFORMATION
#
#-----#

_symmetry_cell_setting      tetragonal
_symmetry_space_group_name_H-M 'P 42/n'
_symmetry_space_group_name_Hall '-P 4bc'
_symmetry_Int_Tables_number 86
loop_
  _symmetry_equiv_pos_as_xyz
  'x, y, z'
  '-x+1/2, -y+1/2, z'
  '-y, x+1/2, z+1/2'
  'y+1/2, -x, z+1/2'
  '-x, -y, -z'
  'x-1/2, y-1/2, -z'
  'y, -x-1/2, -z-1/2'
  '-y-1/2, x, -z-1/2'

_cell_length_a      14.2120(10)
_cell_length_b      14.2120(10)
_cell_length_c      16.6729(14)
_cell_angle_alpha    90

```

_cell_angle_beta	90
_cell_angle_gamma	90
_cell_volume	3367.6(6)
_cell_formula_units_Z	4
_cell_measurement_temperature	100(2)
_cell_measurement_reflns_used	116312
_cell_measurement_theta_min	3
_cell_measurement_theta_max	20

```
#-----#
#
#          CRYSTAL INFORMATION
#
#-----#
```

_exptl_crystal_description	prism
_exptl_crystal_colour	colorless
_exptl_crystal_size_max	0.33
_exptl_crystal_size_mid	0.11
_exptl_crystal_size_min	0.1
_exptl_crystal_density_diffn	1.345
_exptl_crystal_density_method	'not measured'
_exptl_crystal_F_000	1420
_exptl_special_details	

;
10 sec., 0.5 deg., 40 mm
;

```
#-----#
#
#          ABSORPTION CORRECTION
#
#-----#
```

_exptl_absorpt_coefficient_mu	0.709
_exptl_absorpt_correction_type	multi-scan
_exptl_absorpt_process_details	'(SADABS; Bruker, 2007)'
_exptl_absorpt_correction_T_min	0.7996
_exptl_absorpt_correction_T_max	0.9324

```
#-----#
#
#          DATA COLLECTION
#
#-----#
```

_diffrn_ambient_temperature	100(2)
_diffrn_radiation_wavelength	0.71073
_diffrn_radiation_type	MoK\alpha
_diffrn_source	'fine-focus sealed tube'
_diffrn_radiation_monochromator	graphite
_diffrn_measurement_device_type	'Bruker APEXII CCD area-
detector'	

```

_diffrn_measurement_method      '\f and \w scans'
_diffrn_reflns_av_R_equivalents 0.0382
_diffrn_reflns_av_unetI/netI    0.0166
_diffrn_reflns_number           116312
_diffrn_reflns_limit_h_min      -18
_diffrn_reflns_limit_h_max      18
_diffrn_reflns_limit_k_min      -18
_diffrn_reflns_limit_k_max      18
_diffrn_reflns_limit_l_min      -22
_diffrn_reflns_limit_l_max      22
_diffrn_reflns_theta_min        1.88
_diffrn_reflns_theta_max        28.35
_diffrn_reflns_theta_full       25
_diffrn_measured_fraction_theta_full 1
_diffrn_measured_fraction_theta_max 0.995
_reflns_number_total            4189
_reflns_number_gt               3561
_reflns_threshold_expression    >2\s(I)

#-----#
#                                     COMPUTER PROGRAMS USED
#-----#

_computing_data_collection      'APEX2 (Bruker, 2007)'
_computing_cell_refinement      'SAINT (Bruker, 2007)'
_computing_data_reduction       'SAINT (Bruker, 2007)'
_computing_structure_solution   'SHELXS97 (Sheldrick, 1997)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick,
2008)'
_computing_molecular_graphics   'ORTEP-3 for Windows
(Farrugia, 1997)'
_computing_publication_material 'SHELXL-97 (Sheldrick,
1997)'

#-----#
#                                     STRUCTURE SOLUTION
#-----#

_atom_sites_solution_primary    direct
_atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens  geom

#-----#
#                                     REFINEMENT INFORMATION
#-----#

```

```

_refine_special_details
;
  Refinement of F^2^ against ALL reflections. The weighted R-factor
  wR and
  goodness of fit S are based on F^2^, conventional R-factors R are
  based
  on F, with F set to zero for negative F^2^. The threshold
  expression of
  F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc.
  and is
  not relevant to the choice of reflections for refinement. R-
  factors based
  on F^2^ are statistically about twice as large as those based on F,
  and R-
  factors based on ALL data will be even larger.
;
_refine_ls_structure_factor_coef      Fsqd
_refine_ls_matrix_type                full
_refine_ls_weighting_scheme            calc
_refine_ls_weighting_details
      'calc w=1/[\s^2^(Fo^2^)+(0.0358P)^2^+1.9064P] where
P=(Fo^2^+2Fc^2^)/3'
_refine_ls_hydrogen_treatment          mixed
_refine_ls_extinction_method            none
_refine_ls_number_reflns                4189
_refine_ls_number_parameters            225
_refine_ls_number_restraints            8
_refine_ls_R_factor_all                 0.0427
_refine_ls_R_factor_gt                  0.0329
_refine_ls_wR_factor_ref                0.0811
_refine_ls_wR_factor_gt                 0.0776
_refine_ls_goodness_of_fit_ref          1.033
_refine_ls_restrained_S_all             1.032
_refine_ls_shift/su_max                  0
_refine_ls_shift/su_mean                 0
_refine_diff_density_max                 0.309
_refine_diff_density_min                 -0.553
_refine_diff_density_rms                 0.047

#-----#
-----#
#                               ATOMIC TYPES, COORDINATES AND THERMAL PARAMETERS
#
#-----#
-----#

loop_
  _atom_type_symbol
  _atom_type_description
  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
  _atom_type_scatter_source
C C 0.0033 0.0016 'International Tables Vol C Tables 4.2.6.8 and
6.1.1.4'
H H 0 0 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

```

N N 0.0061 0.0033 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
O O 0.0106 0.006 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
Cu Cu 0.3201 1.2651 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

```

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
  _atom_site_symmetry_multiplicity
  _atom_site_calc_flag
  _atom_site_refinement_flags
  _atom_site_disorder_assembly
  _atom_site_disorder_group
C1 C 0.84323(11) 0.12179(11) 0.00335(8) 0.0208(3) Uani 1 1 d . . .
C2 C 0.90732(11) 0.27147(11) -0.02585(8) 0.0209(3) Uani 1 1 d . . .
C3 C 0.98339(11) 0.25191(11) 0.02854(8) 0.0226(3) Uani 1 1 d . . .
H3 H 1.0318 0.297 0.0365 0.027 Uiso 1 1 calc R . .
C4 C 0.98560(11) 0.16896(11) 0.06823(8) 0.0226(3) Uani 1 1 d . . .
C5 C 1.05948(12) 0.14027(13) 0.12740(9) 0.0306(4) Uani 1 1 d . . .
H5A H 1.1098 0.1874 0.1281 0.046 Uiso 1 1 calc R . .
H5B H 1.0856 0.0791 0.1119 0.046 Uiso 1 1 calc R . .
H5C H 1.0314 0.1356 0.1809 0.046 Uiso 1 1 calc R . .
C6 C 0.60109(11) 0.26124(11) -0.25409(8) 0.0228(3) Uani 1 1 d . . .
C7 C 0.68614(11) 0.39885(11) -0.22152(8) 0.0239(3) Uani 1 1 d . . .
C8 C 0.63180(11) 0.44962(11) -0.28005(9) 0.0250(3) Uani 1 1 d . . .
H8 H 0.6426 0.5149 -0.2884 0.03 Uiso 1 1 calc R . .
C9 C 0.56570(11) 0.40443(11) -0.32291(9) 0.0248(3) Uani 1 1 d . . .
C10 C 0.50528(12) 0.44903(13) -0.38593(10) 0.0320(4) Uani 1 1 d . .
.
H10A H 0.5229 0.4245 -0.4388 0.048 Uiso 1 1 calc R . .
H10B H 0.5143 0.5174 -0.385 0.048 Uiso 1 1 calc R . .
H10C H 0.4391 0.4344 -0.3753 0.048 Uiso 1 1 calc R . .
C11 C 0.86064(11) -0.11546(11) 0.13750(8) 0.0238(3) Uani 1 1 d . . .
C12 C 0.88287(12) -0.21682(11) 0.15623(9) 0.0264(3) Uani 1 1 d . . .
H12A H 0.9487 -0.2299 0.1427 0.04 Uiso 1 1 calc R . .
H12B H 0.8417 -0.2579 0.1246 0.04 Uiso 1 1 calc R . .
H12C H 0.8726 -0.2286 0.2135 0.04 Uiso 1 1 calc R . .
N1 N 0.83971(9) 0.20261(9) -0.03765(7) 0.0200(3) Uani 1 1 d . . .
N2 N 0.91497(9) 0.10433(9) 0.05539(7) 0.0220(3) Uani 1 1 d D . .
H2 H 0.9160(13) 0.0521(7) 0.0814(9) 0.026 Uiso 1 1 d D . .
N3 N 0.77711(10) 0.05707(10) -0.00535(8) 0.0266(3) Uani 1 1 d D . .
H3A H 0.7312(9) 0.0695(11) -0.0369(9) 0.032 Uiso 1 1 d D . .
H3B H 0.7778(11) 0.0064(8) 0.0227(9) 0.032 Uiso 1 1 d D . .
N4 N 0.66641(9) 0.30454(9) -0.20953(7) 0.0226(3) Uani 1 1 d . . .
N5 N 0.55114(10) 0.30961(10) -0.30995(7) 0.0243(3) Uani 1 1 d D . .
H5 H 0.5100(10) 0.2793(12) -0.3377(10) 0.029 Uiso 1 1 d D . .
N6 N 0.58389(10) 0.17004(9) -0.24466(8) 0.0257(3) Uani 1 1 d D . .
H6A H 0.6140(11) 0.1397(10) -0.2083(8) 0.031 Uiso 1 1 d D . .

```

H6B H 0.5420(10) 0.1418(10) -0.2732(9) 0.031 Uiso 1 1 d D . .
O1 O 0.89781(8) 0.34668(7) -0.06382(6) 0.0243(2) Uani 1 1 d . . .
O2 O 0.75111(8) 0.43405(8) -0.18057(6) 0.0287(3) Uani 1 1 d . . .
O3 O 0.92212(8) -0.05386(8) 0.15192(7) 0.0291(3) Uani 1 1 d . . .
O4 O 0.77946(9) -0.09556(9) 0.10989(7) 0.0328(3) Uani 1 1 d . . .
Cu1 Cu 0.75 0.25 -0.122791(13) 0.01769(8) Uani 1 2 d S . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
C1 0.0244(7) 0.0237(8) 0.0144(6) 0.0001(5) -0.0017(5) 0.0017(6)
C2 0.0257(8) 0.0238(8) 0.0132(6) -0.0015(5) 0.0039(5) -0.0002(6)
C3 0.0231(8) 0.0269(8) 0.0179(6) -0.0010(5) 0.0008(5) -0.0044(6)
C4 0.0211(7) 0.0295(8) 0.0172(6) 0.0000(6) 0.0003(5) -0.0013(6)
C5 0.0253(8) 0.0373(10) 0.0293(8) 0.0064(7) -0.0081(6) -0.0051(7)
C6 0.0251(8) 0.0288(8) 0.0145(6) 0.0038(5) 0.0067(5) 0.0124(6)
C7 0.0302(8) 0.0260(8) 0.0156(6) 0.0032(5) 0.0077(6) 0.0110(6)
C8 0.0299(8) 0.0245(8) 0.0205(7) 0.0077(6) 0.0072(6) 0.0100(6)
C9 0.0257(8) 0.0293(8) 0.0193(6) 0.0087(6) 0.0089(6) 0.0122(7)
C10 0.0299(9) 0.0364(10) 0.0296(8) 0.0142(7) -0.0006(7) 0.0097(7)
C11 0.0275(8) 0.0268(8) 0.0172(6) 0.0050(5) -0.0043(5) -0.0017(6)
C12 0.0268(8) 0.0260(8) 0.0264(7) -0.0002(6) -0.0059(6) -0.0006(7)
N1 0.0248(7) 0.0211(6) 0.0140(5) 0.0003(4) -0.0014(4) 0.0010(5)
N2 0.0249(7) 0.0242(7) 0.0170(5) 0.0047(5) -0.0038(5) -0.0016(5)
N3 0.0314(7) 0.0247(7) 0.0238(6) 0.0088(5) -0.0118(5) -0.0052(6)
N4 0.0296(7) 0.0234(7) 0.0146(5) 0.0033(5) 0.0029(5) 0.0110(5)
N5 0.0272(7) 0.0287(7) 0.0169(6) 0.0056(5) 0.0025(5) 0.0082(6)
N6 0.0329(8) 0.0263(7) 0.0180(6) 0.0038(5) -0.0028(5) 0.0084(6)
O1 0.0310(6) 0.0231(6) 0.0187(5) 0.0021(4) 0.0026(4) -0.0006(5)
O2 0.0363(7) 0.0281(6) 0.0218(5) 0.0024(4) 0.0007(5) 0.0089(5)
O3 0.0294(6) 0.0280(6) 0.0298(6) 0.0067(5) -0.0092(5) -0.0049(5)
O4 0.0289(6) 0.0331(7) 0.0365(6) 0.0135(5) -0.0134(5) -0.0034(5)
Cu1 0.02490(14) 0.01643(13) 0.01175(12) 0 0 0.00403(10)