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Intermolecular Watson–Crick-like ligand pairing in two Cu(II) compounds with the ligand bis(pyrimidin-2-yl)amine forming 2D chain-type compounds

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Abstract

Two unusual copper(II) compounds with formule $[Cu(dipm)(HCOO)_2(H_2O)]$ (**1**) and $[Cu(dipm)(C_2O_4)(H_2O)]$ (**2**) (in which dipm = bis(pyrimidin-2-yl)amine) have been synthesized and characterised by X-ray crystallography, spectroscopy and EPR. The geometry around the Cu(II) ion in compound **1** is distorted octahedral with the basal plane formed by two nitrogen atoms of a ligand molecule with Cu–N distances of 1.992(2), 2.040(2) Å and two oxygen atoms of two formato anions with Cu–O distances of 1.948(2), 1.984(2) Å. The axial positions are occupied by an oxygen atom of the water molecule (Cu–O distance 2.195(2) Å) and by the second oxygen atom of one of the formato molecules at a semi-coordinating distance of 2.711(2) Å. The geometry around the Cu(II) in compound **2** is square pyramidal with the basal plane occupied by two nitrogen atoms of a ligand molecule (Cu–N distances of 2.007(3), 2.015(3) Å) and two oxygen atoms of the oxalato anion (Cu–O distances of 1.955(3), 1.956(2) Å). The fifth position is occupied by an oxygen atom of the water molecule with a Cu–O distance of 2.246(3) Å.

The 2D chain of H-bonds consists of intermolecular built hydrogen bonds between 2 dipm ligands of the Watson–Crick-type and H-bonds between the water molecules and the formato (compound **1**), or oxalato anions (compound **2**). In addition, stacking interactions between dipm ligands are present in both compounds (ring–ring distances 3.6–3.8 Å).

Keywords: Crystal structure; Copper; Hydrogen bond; Formato; Oxalato

In the field of supramolecular interactions of coordination compounds, not only the direct metal-ligand bonds are of interest, but also hydrogen bonding is of great importance [1–9].

A ligand with interesting hydrogen-bonding properties is the recently developed ligand bis(pyrimidin-2-yl)amine (abbreviated as dipm) [10–14]. The dipm molecule can both donate and accept hydrogen bonds, and has a more or less linear donor–acceptor array of the A–D–A type. This type of array is capable of forming the so-called Watson–Crick-type hydrogen bonds, similar to the one reported for the first generation ligand 2-aminopyrimidine [15,16]. So far only a few X-ray crystal structures of Cu(II) compounds with dipm have been published, i.e. $[Cu(dipm)(CO_3)(H_2O)](H_2O)_2$ [10], $[Cu(dipm)_2(dicyanamide)(CF_3SO_3)](C_2H_6O)_{1/2}$ [11] $[\mu\text{–}Cl\text{–}CuCl(dipm)]_n$ [12], $[Cu(dipm)_2(H_2O)_2](dipm)_2(H_2O)_2(CF_3SO_3)_2$ and $[Cu(dipm)_2(H_2O)_2](ClO_4)_2$ [14].

In this study, the synthesis, crystal structure and characterisation of two new Cu(II) compounds with the formule $[Cu(dipm)(HCOO)_2(H_2O)]$ (**1**) and $[Cu(dipm)(C_2O_4)(H_2O)]$ (**2**) have been performed. Both compounds are mononuclear based. Due to the difference in anion (formato and oxalato), the lattice packing differs and each compound displays interesting H-bonding properties.

Blue (compound **1**) or green (compound **2**) crystals were obtained by adding the appropriate copper(II) salt to the ligand in an ethanol/water mixture [17]. A plot showing

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the numbering scheme and bond lengths and bond angles for the X-ray crystallographic analysis [18] is shown in Figs. 1 and 2 for compounds **1** and **2**, respectively.

The basal plane of the mononuclear unit of [Cu(dipm)-$(HCOO)_2(H_2O)$] (**1**) is occupied by two nitrogen atoms of a ligand molecule with Cu–N distances of 1.992(2), 2.040(2) Å and two oxygen atoms of two formato anions

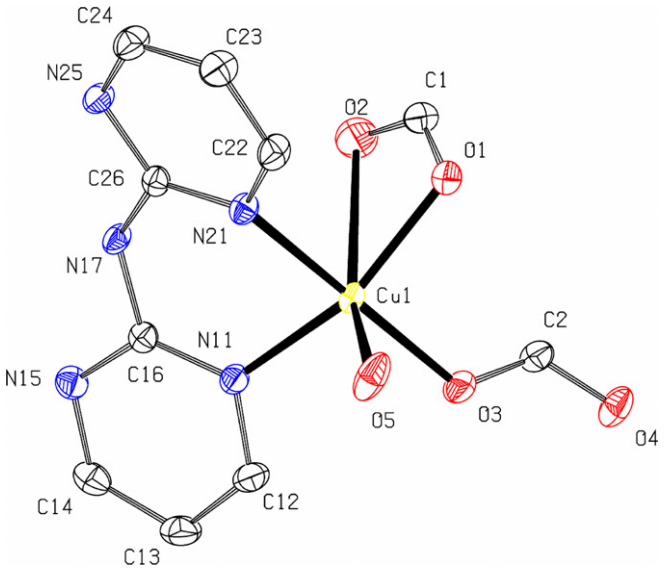

Fig. 1. Thermal ellipsoid plot (50% probability) of [Cu(dipm)$(HCOO)_2(H_2O)$] (**1**) showing the crystallographic numbering scheme. Selected bond distances (Å) and bond angles (°): Cu(1)–O(3) 1.948(2), Cu(1)–O(1) 1.984(2), Cu(1)–N(21) 1.992(2), Cu(1)–N(11) 2.040(2), Cu(1)–O(5) 2.195(2), Cu(1)–O(2) 2.711(2), O(3)–Cu(1)–N(21) 176.92(7), O(1)–Cu(1)–N(11) 152.53(7), O(1)–Cu(1)–O(5) 104.45(7), O(2)–Cu(1)–O(5) 156.74(7).

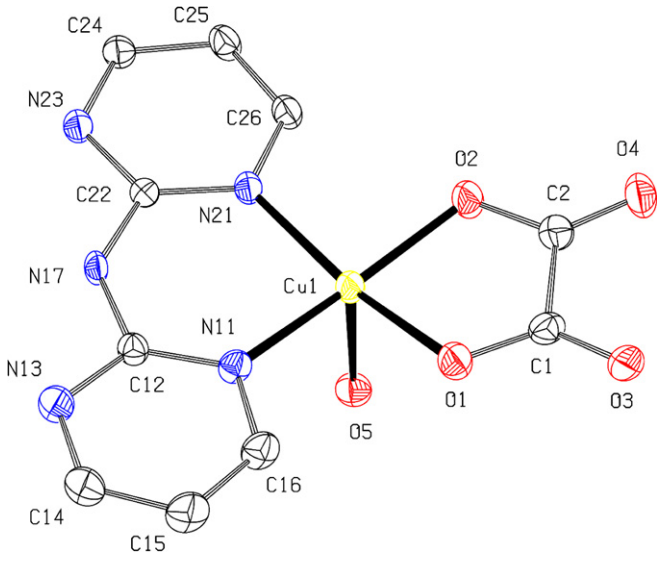

Fig. 2. Thermal ellipsoid plot (50% probability) of [Cu(dipm)$(C_2O_4)(H_2O)$] (**2**) showing the crystallographic numbering scheme. Cu(1)–O(1) 1.955(3), Cu(1)–O(2) 1.956(2), Cu(1)–N(11) 2.007(3), Cu(1)–N(21) 2.015(3), Cu(1)–O(5) 2.246(3), O(2)–Cu(1)–N(11) 168.52(9), O(1)–Cu(1)–N(21) 168.84(9), O(1)–Cu(1)–O(5) 97.31(10).

with Cu–O distances of 1.948(2) and 1.984(2) Å. The axial position is occupied by an oxygen atom of the water molecule with a Cu–O distance of 2.195(2) Å. The other axial position is occupied by a second oxygen atom of one of the formato molecules at a semi-coordinating distance of 2.711(2) Å. As the basal angles are 176.92(7) and 152.53(7)°, the geometry can be described as tetrahedrally distorted octahedral.

The crystal-lattice of the compound is stabilised by stacking between pyrimidine rings with a ring–ring distance of 3.592 Å and by an interesting hydrogen-bonding system (vide infra) in which 2 ligands form a Watson–Crick-type pair.

The basal plane of [Cu(dipm)$(C_2O_4)(H_2O)$] (**2**) is occupied by two nitrogen atoms of a ligand molecule with Cu–N distances of 2.007(3), 2.015(3) Å and two oxygen atoms of the oxalato anion with Cu–O distances of 1.955(3) and 1.956(2) Å. The fifth position is occupied by an oxygen atom of the water molecule with a Cu–O distance of 2.246(3) Å. The geometry of 5-coordinated compounds can be described by the parameter $\tau(\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles, $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry) [22]. As in this case, the basal angles are 168.52(9) and 168.84(9) and consequently $\tau = 0$, the geometry around the Cu(II) ion is square pyramidal. The lattice of the compound is stabilised by stacking between the pyrimidine rings with a distance of 3.895 Å and by an interesting hydrogen-bonding system (vide infra), like for the formato compound (**1**). The distances and angles are in agreement with the related compound [Cu(di-2-pyridylamine)$(C_2O_4)(H_2O)$](H_2O), although this compound has a slightly distorted SP geometry ($\tau = 0.1$) [23].

A clear hydrogen bond interaction of the Watson–Crick-type is observed between the amine N atom of the coordinated dipm ligand and a pyrimidyl N atom of the non-coordinating dipm ligand with N···N distances of 2.976(2) and 3.019(5) Å, for compounds **1** and **2**, respectively. This type of hydrogen bond array has been observed earlier with this ligand [10–12,14]. Secondly, medium to strong hydrogen bonds are formed by the hydrogen atoms of the coordinated water molecule to the oxygen atoms of the formato anion (compound **1**), and to the oxalato anion (compound **2**) with O···O distances of 2.799(3), 2.766(2) Å for compound **1** and from 2.732(4) to 3.125(4) for compound **2**. In this way, in both cases a two-dimensional layer is formed, which is schematically depicted in Figs 3 and 4, for compounds **1** and **2**, respectively. Details of the hydrogen bondings are given in Table S1 and S2.

In the IR spectrum [24], a broad band of medium intensity is observed at 3344 cm^{-1} in compound **1** and at 3391 cm^{-1} in compound **2**, which can tentatively be assigned to the OH vibration of the hydrogen-bonded water molecules. The NH vibration, which is observed at 3230 cm^{-1} in the free ligand, is now observed at 3247 cm^{-1} in compound **1** and as a split band at 3256, 3220 cm^{-1} for compound **2**.