# Diversity of supramolecular aggregation in copper(II) pentane-2,4-dionato compounds with methyl substituted 2-aminopyridines

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# Diversity of supramolecular aggregation in copper(II) pentane-2,4-dionato compounds with methyl substituted 2-aminopyridines

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Three copper(II) bis(pentane-2,4-dionato-$\kappa^2 O,O'$) compounds with 2-amino-3-methylpyridine (2,3-ampy) (**1**), 2-amino-5-methylpyridine (2,5-ampy) (**2**), and 2-amino-4-methylpyridine (2,4-ampy) (**3**) were prepared by reaction of bis(pentane-2,4-dionato-$\kappa^2 O,O'$)copper(II) with selected methyl substituted 2-aminopyridines. The coordination of Cu(II) in all three compounds is square pyramidal and intramolecular N–H · · · O hydrogen-bonding is present. X-ray crystallographic studies reveal different crystal aggregation influenced by a methyl substituent on pyridine. No intermolecular N–H · · · O hydrogen-bonding is present in **1**. Intermolecular N–H · · · O hydrogen-bonding in **2** forms infinite chains and dimers are formed in **3**. Extended 3-D aggregation was found in **2** *via* $\pi$–$\pi$ and C–H · · · $\pi$ (arene) interactions, while only chain formation was found in **1** and **3**.

*Keywords*: Acetylacetonate; Copper; Crystal structure; Hydrogen bonds; $\pi$–$\pi$ Interaction

## 1. Introduction

Solid-state arrangement within a crystal is a central challenge of materials chemistry and control of coordination chemistry is essential in inorganic crystal engineering [1]. There is considerable interest also in non-covalent intermolecular interactions such as hydrogen bonds and $\pi$–$\pi$ interactions as means for assembly of metal complexes into extended networks [1, 2]. Direction-specific intermolecular forces which influence the molecular arrangements in the solid state are very often comparatively weak and the interpretation and prediction of crystal arrangement remains difficult [3, 4]. Metal complexes of $\beta$-diketonate ligands attract interest in solid-state supramolecular chemistry mostly due to promise for the design of porous and supramolecular materials with interesting electronic, magnetic, and optical properties [5–9]. Furthermore, metal complexes of $\beta$-diketonate derivatives can be good precursors in metal–organic chemical vapor deposition [10]. Cu(II) $\beta$-diketonate compounds display varied coordination chemistry, ranging from square planar, square pyramidal to octahedral,

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depending mostly on $\beta$-diketonate ligands and also on the presence of the additional ligands [5, 6]. When $Cu(acac)_2$ interacts with additional ligand, five coordination is predominant. Only two crystal structures are known with octahedral coordination of copper, $Cu(acac)_2(L)_2$ [11, 12]. The electron-withdrawing influence of additional fluorines on $\beta$-diketonato ligands enhances the acid character of the central copper and octahedral coordination can be achieved [5, 13–16]. The reported bis(pentane-2,4-dionato-$O,O'$)copper(II) compounds with 2-aminopyridines bearing just one methyl group on positions 3, 4, or 5 provide insight on the influence of a methyl group on $\pi$–$\pi$ interactions and hydrogen-bond formation.

## 2. Experimental

### 2.1. *Materials and characterization*

2-Amino-3-methylpyridine, 2-amino-4-methylpyridine, and 2-amino-5-methylpyridine were purchased from Fluka; chloroform was purchased from Merck. All chemicals and solvents were of reagent grade and used as purchased. $Cu(acac)_2$ was synthesized according to the literature procedure [17]. Infrared (IR) spectra of the solid samples (4000–600 $cm^{-1}$) were recorded using a Perkin-Elmer Spectrum 100 equipped with a Specac Golden Gate Diamond ATR as a solid sample support. Elemental (C, H, and N) analysis was obtained using a Perkin-Elmer Elemental Analyzer 2400 CHN.

### 2.2. *General synthesis*

$Cu(acac)_2$ (0.065 g, 0.25 mmol) was dissolved in warm chloroform (5 mL) and 2-amino-3-methylpyridine (0.027 g, 0.25 mmol) for **1**, 2-amino-5-methylpyridine (0.027 g, 0.25 mmol) for **2**, and 2-amino-4-methylpyridine (0.027 g, 0.25 mmol) for **3** added. The reaction mixture was stirred for 5 min and then allowed to stand at room temperature. Blue crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent. Compound **1**: (yield: 0.055 g, 59%) Anal. Calcd [$Cu(acac)_2$(2,3-ampy)] ($C_{16}H_{22}CuN_2O_4$) (MW = 369.90): C 51.95, H 5.99, N 7.57; found C 51.95, H 6.10, N 7.49. IR (ATR, $cm^{-1}$): 3471w, 3371w, 1738 m, 1633w, 1577s, 1518s, 1457s, 1347s, 1366 m, 1273 m, 1203 m, 1017 m, 931 m, 775 m, 757 m, 678w, 654w. Compound **2**: (yield: 0.061 g, 66%) Anal. Calcd [$Cu(acac)_2$(2,5-ampy)] ($C_{16}H_{22}CuN_2O_4$) (MW = 369.90): C 51.95, H 5.99, N 7.57; found C 51.90, H 6.33, N 7.76. IR (ATR, $cm^{-1}$): 3466w, 3368w, 1640w, 1578s, 1519s, 1506s, 1398s, 1353 m, 1272 m, 1018 m, 933 m, 810 m, 781 m, 772 m, 676w, 655 m. Compound **3**: (yield: 0.067 g, 72%) Anal. Calcd [$Cu(acac)_2$(2,4-ampy)] ($C_{16}H_{22}CuN_2O_4$) (MW = 369.90): C 51.95, H 5.99, N 7.57; found C 51.93, H 6.30, N 7.60. IR (ATR, $cm^{-1}$): 3458w, 3358w, 1738s, 1638w, 1575 m, 1554 m, 1518s, 1373s, 1276 m, 1217 m, 1019 m, 932 m, 811 m, 781 m, 782 m, 678w, 657w.

### 2.3. *X-ray structure determination*

Single-crystal X-ray diffraction data were collected at room temperature with a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The data were processed using DENZO [18]. Structures were solved by

Table 1. Crystallographic data for **1–3**.

| Parameter | [Cu(acac)$_2$(2,3-ampy)] (**1**) | [Cu(acac)$_2$(2,5-ampy)] (**2**) | [Cu(acac)$_2$(2,4-ampy)] (**3**) |
|---|---|---|---|
| Empirical formula | C$_{16}$H$_{22}$CuN$_2$O$_4$ | C$_{16}$H$_{22}$CuN$_2$O$_4$ | C$_{16}$H$_{22}$CuN$_2$O$_4$ |
| Formula weight | 369.90 | 369.90 | 369.90 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | | | |
| $a$ | 7.9276(3) | 7.5588(2) | 8.4076(2) |
| $b$ | 8.1441(2) | 8.2690(3) | 10.5661(3) |
| $c$ | 13.6842(4) | 14.3711(4) | 11.7169(3) |
| $\alpha$ | 89.677(2) | 94.037(2) | 111.304(2) |
| $\beta$ | 78.928(2) | 104.503(2) | 105.484(2) |
| $\gamma$ | 88.975(2) | 91.428(2) | 101.0650(10) |
| Volume (Å$^3$), $Z$ | 866.91(5), 2 | 866.62(5), 2 | 884.84(4), 2 |
| Calculated density (Mg m$^{-3}$) | 1.417 | 1.418 | 1.388 |
| Absorption coefficient (mm$^{-1}$) | 1.280 | 1.280 | 1.254 |
| $F(000)$ | 386 | 386 | 386 |
| Extinction coefficient | – | – | 0.071(7) |
| Crystal size (mm$^3$) | 0.30 × 0.15 × 0.13 | 0.60 × 0.58 × 0.13 | 0.60 × 0.50 × 0.25 |
| Reflections collected | 6030 | 6700 | 6913 |
| Independent reflections | 3930 [$R$(int) = 0.0196] | 3841 [$R$(int) = 0.0289] | 4004 [$R$(int) = 0.0211] |
| Parameters | 213 | 213 | 214 |
| Goodness-of-fit on $F^2$, $S^c$ | 1.030 | 1.040 | 1.046 |
| Final $R$ indices [$I > 2\sigma(I)$][a] | $R_1 = 0.0346$, $wR_2 = 0.0915$ | $R_1 = 0.0381$, $wR_2 = 0.1067$ | $R_1 = 0.0354$, $wR_2 = 0.0985$ |
| $R$ indices (all data)[b] | $R_1 = 0.0436$, $wR_2 = 0.0979$ | $R_1 = 0.0426$, $wR_2 = 0.1109$ | $R_1 = 0.0409$, $wR_2 = 0.1052$ |

[a]$R_1 = \sum F_o - F_c / \sum F_o$. [b]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c]$S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where $n$ is the number of reflections and $p$ is the total number of parameters refined.

direct methods implemented in SIR-97 [19] and refined by full-matrix least-squares based on $F^2$ with SHELXL-97 [20]. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were initially located in difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C–H = 0.93 (aromatic and alkenyl) or 0.96 Å (CH$_3$), and N–H = 0.86 Å and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for methyl groups, which were permitted to rotate but not tilt, and 1.2 for all other H atoms. To improve the refinement results, four reflections in the case of **2** and one reflection in the case of **3** with too high value of $\delta(F^2)$/e.s.d. and with $F_o^2 < F_c^2$ were deleted from the refinement. The crystallographic data are listed in table 1.

## 3. Results and discussion

### 3.1. *Molecular structures of 1–3*

All three compounds crystallize in triclinic $P\bar{1}$ space groups with small variations in cell parameters between **1** and **2**, while cell parameters in **3** are significantly different. Compounds **1–3** have square-pyramidal molecular structures (figure 1). In the basal

plane copper is surrounded by four oxygen atoms of two chelating 2,4-pentanedionato ligands with Cu–O distances 1.929–1.950 Å in all three compounds (tables 2–4). Bite angles O–Cu–O in all compounds are within the range 92.51°–93.49°, while O–Cu–O in *trans* positions are 166.19°–169.49° (tables 2–4). These angles are within typical values for $\beta$-diketonate compounds [13, 21, 22].
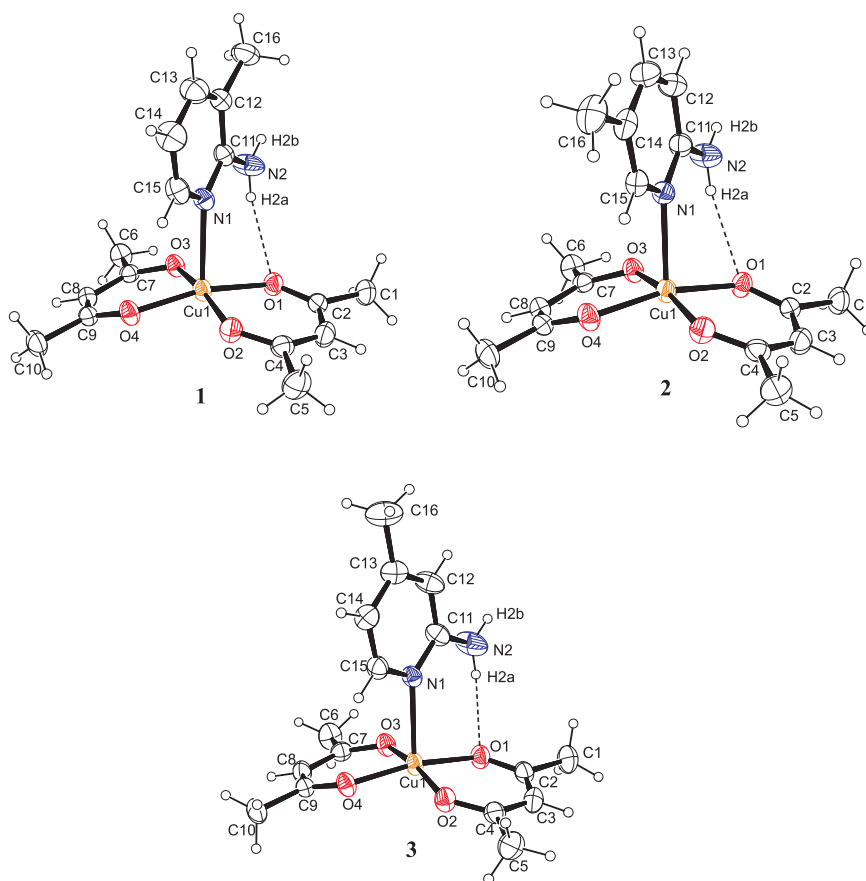


Figure 1. Molecular structures of **1–3** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular hydrogen bond is indicated by a dashed line.

Table 2. Selected bond distances and angles for **1**.

| Cu1–O1 | 1.9481(14) | Cu1–O4 | 1.9355(14) |
|---|---|---|---|
| Cu1–O2 | 1.9419(15) | Cu1–N1 | 2.3412(18) |
| Cu1–O3 | 1.9338(14) | | |
| | | | |
| O3–Cu1–O4 | 93.49(6) | O2–Cu1–O1 | 92.84(6) |
| O3–Cu1–O2 | 169.46(7) | O3–Cu1–N1 | 92.81(6) |
| O4–Cu1–O2 | 84.91(6) | O4–Cu1–N1 | 98.86(6) |
| O3–Cu1–O1 | 86.37(6) | O2–Cu1–N1 | 97.74(6) |
| O4–Cu1–O1 | 166.91(7) | O1–Cu1–N1 | 94.21(6) |

Table 3.   Selected bond distances and angles for **2**.

| | | | |
|---|---|---|---|
| Cu1–O1 | 1.9504(14) | Cu1–O4 | 1.9413(14) |
| Cu1–O2 | 1.9503(15) | Cu1–N1 | 2.3061(17) |
| Cu1–O3 | 1.9391(15) | | |
| O3–Cu1–O4 | 93.13(6) | O2–Cu1–O1 | 92.51(6) |
| O3–Cu1–O2 | 168.49(7) | O3–Cu1–N1 | 94.29(6) |
| O4–Cu1–O2 | 85.12(7) | O4–Cu1–N1 | 96.91(7) |
| O3–Cu1–O1 | 86.48(6) | O2–Cu1–N1 | 97.21(6) |
| O4–Cu1–O1 | 166.19(7) | O1–Cu1–N1 | 96.88(6) |

Table 4.   Selected bond distances and angles for **3**.

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.9350(15) | Cu(1)–O(4) | 1.9287(14) |
| Cu(1)–O(2) | 1.9449(15) | Cu(1)–N(1) | 2.3694(17) |
| Cu(1)–O(3) | 1.9475(15) | | |
| O4–Cu1–O1 | 169.24(7) | O2–Cu1–O3 | 167.91(7) |
| O4–Cu1–O2 | 85.69(6) | O4–Cu1–N1 | 94.88(6) |
| O1–Cu1–O2 | 92.88(7) | O1–Cu1–N1 | 95.87(6) |
| O4–Cu1–O3 | 93.36(6) | O2–Cu1–N1 | 97.04(6) |
| O1–Cu1–O3 | 85.80(7) | O3–Cu1–N1 | 95.04(6) |

The copper lies above the plane formed by four pentane-2,4-dionato oxygen atoms by 0.199 Å in **1**, 0.214 Å in **2**, and 0.193 Å in **3**. Fifth coordination site is occupied by the additional ligand in the axial position. The geometry is square pyramidal with only slight distortion. The distortion of a square pyramid can be best described by the structural parameter $\tau$ ($\tau = 0$ for an ideal square pyramid and $\tau = 1$ for an ideal trigonal bipyramid [23]), which in this case has values of 0.04 for **1** and **2**, and 0.02 for **3**. The Cu–N bond lengths vary about 0.06 Å, 2.3412(18) Å in **1**, 2.3061(17) Å in **2**, and 2.3694(17) Å in **3**. These values are significantly greater than in Cu(acac)$_2$(4-dimethylaminopyridine-$N$) (2.119 Å) [24], but are similar to Cu(acac)$_2$ complexes with adenine, quinoline, and *iso*-nicotinamide, where the bond lengths are 2.328 [25], 2.357 [26], and 2.384 Å [13], respectively.

In all compounds two acetylacetonato ligands are not coplanar. The angle formed between Cu1–O1–C2–C3–C4–O2 and Cu1–O3–C7–C8–C9–O4 chelate rings is 25.09(7)° in **1**, 30.12(7)° in **2**, and the smallest angle of 22.00(9)° is found in **3**. Pyridine ring is not perpendicular to O1–O2–O3–O4 plane, but forms an angle of 86.61° in **1**, 84.76° in **2**, and 85.54° in **3**. Furthermore, pyridine ring in all three compounds is slightly rotated toward O1 as can be seen by comparing the torsion angle O1–Cu1–N1–C11 and O3–Cu1–N1–C11 (39.20(17)°, −47.36(17)° in **1**, 41.02(17)°, −45.95(17)° in **2**, and 23.68(19)°, −62.61(18)° in **3**, respectively), with the largest rotation observed in **3**. Due to this rotation the amino group forms an intramolecular hydrogen bond only with O1, not with O4 (table 5) with the graph-set motif $S(6)$ [27].

### 3.2. Crystal aggregation of 1

Although reported compounds have similar molecular structures, the crystal aggregation is influenced by the presence of a methyl substituent on different positions of 2-aminopyridine. The amino group of 2,3-ampy in **1** is not involved in any

Table 5. Hydrogen bonds and C–H···$\pi$(arene) interactions for **1–3** (Å and °).

| D–H···A | $d$(D–H) | $d$(H···A) | $d$(D···A) | ∠(DHA) | Symmetry transformation for acceptors |
|---|---|---|---|---|---|
| **1** | | | | | |
| N2–H2A···O1 | 0.86 | 2.30 | 3.037(3) | 144.3 | *x, y, z* |
| **2** | | | | | |
| N2–H2A···O1 | 0.86 | 2.35 | 3.095(3) | 144.5 | *x, y, z* |
| N2–H2B···O2 | 0.86 | 2.56 | 3.303(2) | 145.6 | *1 − x, y, z* |
| N2–H2B···O4 | 0.86 | 2.57 | 3.290(3) | 141.5 | *1 − x, y, z* |
| C1–H1C···*Cg*1 | 0.96 | 3.00 | 3.854(3) | 149.0 | *x, 1 + y, z* |
| **3** | | | | | |
| N2–H2A···O1 | 0.86 | 2.16 | 2.965(3) | 155.8 | *x, y, z* |
| N2–H2B···O3 | 0.86 | 2.46 | 3.229(2) | 150.0 | *1 − x, 2 − y, 2 − z* |

*Cg*1 is a Cu1/O3/C7–C9/O4 ring centroid.

intermolecular N–H···O hydrogen-bonding, probably due to the steric bulk of the methyl on position 3 in 2,3-ampy ligand. Strong $\pi$–$\pi$ interactions are present between two parallel neighboring Cu1–O3–C7–C8–C9–O4 chelate rings with a $Cg1\cdots Cg1(-x, -y, 2-z)$ centroid–centroid distance of 3.4654(10) Å, a perpendicular distance from the centroid $Cg1$ to the plane of the other ring of 3.4056(7) Å and a centroid offset of 0.641 Å (figure 2). The 2-amino-3-methylpyridine is also involved in strong $\pi$–$\pi$ interactions between two parallel neighboring pyridine rings with a $Cg2\cdots Cg2(1-x, -y, 1-z)$ centroid–centroid distance of 3.7300(14) Å, a perpendicular distance from the centroid $Cg2$ to the plane of the other ring of 3.5975(10) Å and a centroid offset of 0.985 Å. Due to this interaction a chain is formed (figure 2). The distance between copper and C8 of the neighboring molecule $Cu1\cdots C8(-x, -y, 2-z)$ is 3.451(2) Å.

Observed $\pi$–$\pi$ interactions are consistent with well-defined $\pi$–$\pi$ stacking interactions [28–31], although the interplanar separations are somewhat greater than the graphite spacing of 3.35 Å [32]. Janiak classified such interactions in nitrogen containing heteroaromatic compounds as strong interactions since rather short centroid–centroid contacts ($Cg\cdots Cg < 3.8$ Å), small slip angles ($<25°$) and small vertical displacements ($<1.5$ Å) translate into a sizeable overlap of the aromatic planes. In comparison, medium-to-weak interactions exhibit rather long centroid–centroid distances ($>4.0$ Å) together with large slip angles ($>30°$) and large vertical displacements ($>2.0$ Å) [33–35]. Short $Cu\cdots C_\gamma$ distances are common in square-planar Cu($\beta$-diketonato)$_2$ compounds as summarized by Gromilov and Baidina [21]. The shortest $Cu\cdots C_\gamma$ distances of 3.01 Å and 3.06 Å were found in *trans*-bis(benzoylacetonato)copper(II) and Cu(acac)$_2$, respectively [36, 37]. In these two compounds centroid–centroid contacts are 3.13 Å and 3.14 Å with the angle between metallacycles being 0.02°, respectively. In bis(3-benzylpentane-2,4-dionato)copper(II), $Cu\cdots C_\gamma$ and centroid–centroid distances between parallel metallacycles are 3.26 Å and 3.22 Å, respectively [38]. Short $Cu\cdots C_\gamma$ distances and $\pi$–$\pi$ interactions are also present in some square-pyramidal compounds of copper(II) $\beta$-diketonates. The shortest interactions were found in *catena*-(3-cyanopentane-2,4-dionato-*O,O′,N*)(3-cyanopentane-2,4-dionato-*O,O′*)copper(II) [39] and (4-cyanopyridine)-*cis*-bis(1,1,1-trifluoropentane-2,4-dionato)copper(II) [14] with centroid–centroid contacts between two parallel metallacycles of 3.16 Å and 3.24 Å and with $Cu\cdots C_\gamma$ distances of 3.33 Å and 3.26 Å, respectively, and in
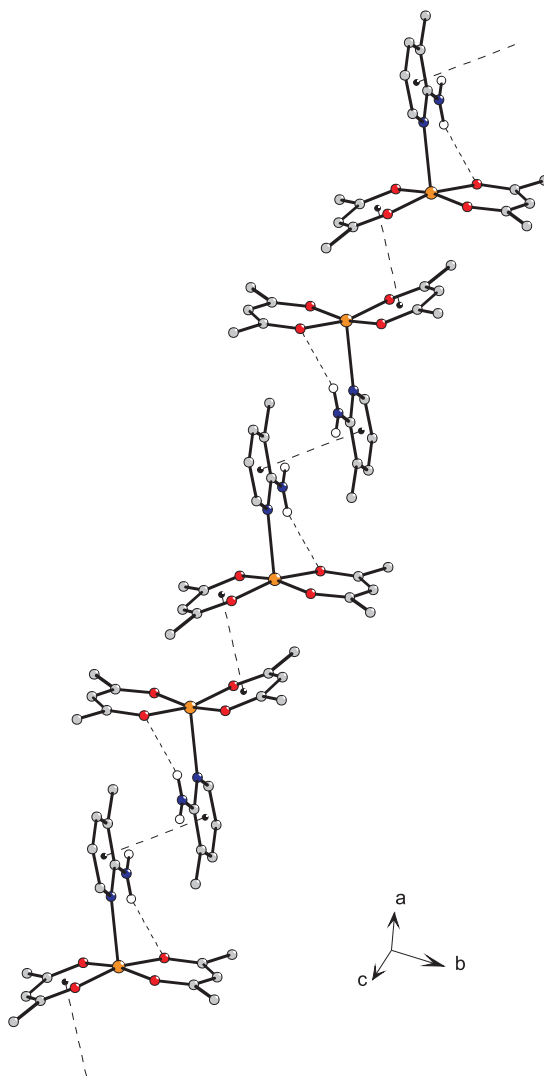
Figure 2. Chain formation in **1**. Dashed lines indicate intramolecular hydrogen bonds and $\pi$–$\pi$ interactions. For clarity, hydrogen atoms not involved in the motif shown have been omitted.

Cu(acac)$_2$(adenine-$N^7$) ethanol solvate with centroid–centroid contact of 3.23 Å with the angle between metallacycles 0.02° and Cu$\cdots$C$_\gamma$ distance of 3.23 Å [25]. Centroid–centroid distances in the range 3.27 Å–3.49 Å with parallel metallacycles or deviating from planarity by up to 0.03° and with Cu$\cdots$C$_\gamma$ distances in the range from 3.30 Å to 3.46 Å were observed in several examples [14–16, 22, 25, 26, 40–43].

### 3.3. *Crystal aggregation of 2*

Compound **2** with 2-amino-5-methylpyridine exhibits the most extended non-covalent aggregation compared to the other two compounds. A chain of molecules is formed due
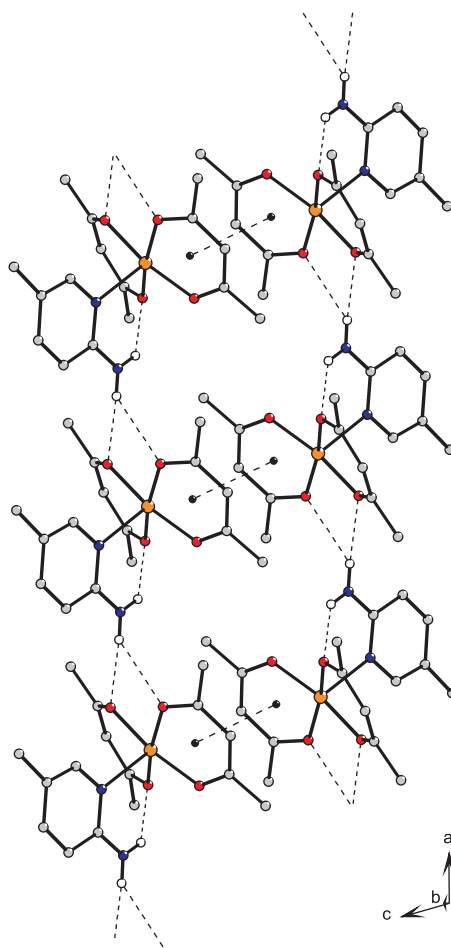
Figure 3. Chain formation in **2**. Dashed lines indicate hydrogen bonds and $\pi$–$\pi$. For clarity, hydrogen atoms not involved in the motif shown have been omitted.

to the intermolecular bifurcated hydrogen-bonding N2–H2B$\cdots$O2$(1 - x,\ y,\ z)$ and N2–H2B$\cdots$O4$(1 - x, y, z)$ with the graph-set motif $C_1^2(6)[R_1^2(4)]$ (figure 3). Square-pyramidal **2** is involved in strong $\pi$–$\pi$ interactions between two parallel neighboring Cu1–O3–C7–C8–C9–O4 chelate rings with a $Cg1 \cdots Cg1$ $(2 - x, 1 - y, 1 - z)$ centroid–centroid distance of 3.6272(10) Å, a perpendicular distance from the centroid $Cg1$ to the plane of the other ring of 3.5062(7) Å and a centroid offset of 0.929 Å (figure 3). These values are somewhat larger than in **1**, also causing an elongation of the Cu1$\cdots$C8 $(-x, 1 - y, 2 - z)$ distance (3.614 Å).

Chains are arranged into layers *via* medium strong $\pi$–$\pi$ interactions between two parallel neighboring pyridine rings with a $Cg2 \cdots Cg2$ $(2 - x, 1 - y, 1 - z)$ centroid–centroid distance of 4.0254(14) Å, a perpendicular distance from the centroid $Cg2$ to the plane of the other ring of 3.5374(9) Å and a centroid offset of 1.921 Å (figure 4). Further aggregation is achieved by weak C1–H1C$\cdots$Cg1 $(x, 1 + y, z)$ interactions connecting layers into an extended 3-D network (figure 5).
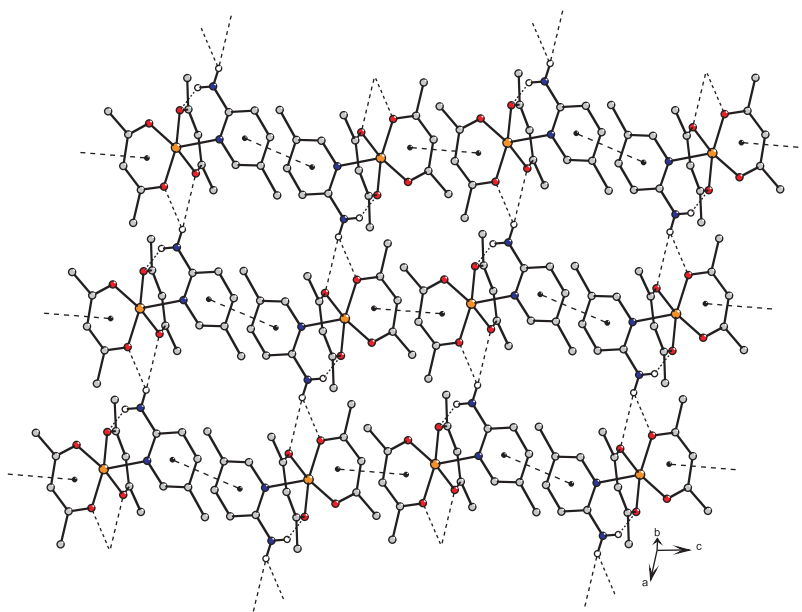
Figure 4.   Layer formation in **2**. Dashed lines indicate hydrogen bonds and π–π interactions. For clarity, hydrogen atoms not involved in the motif shown have been omitted.
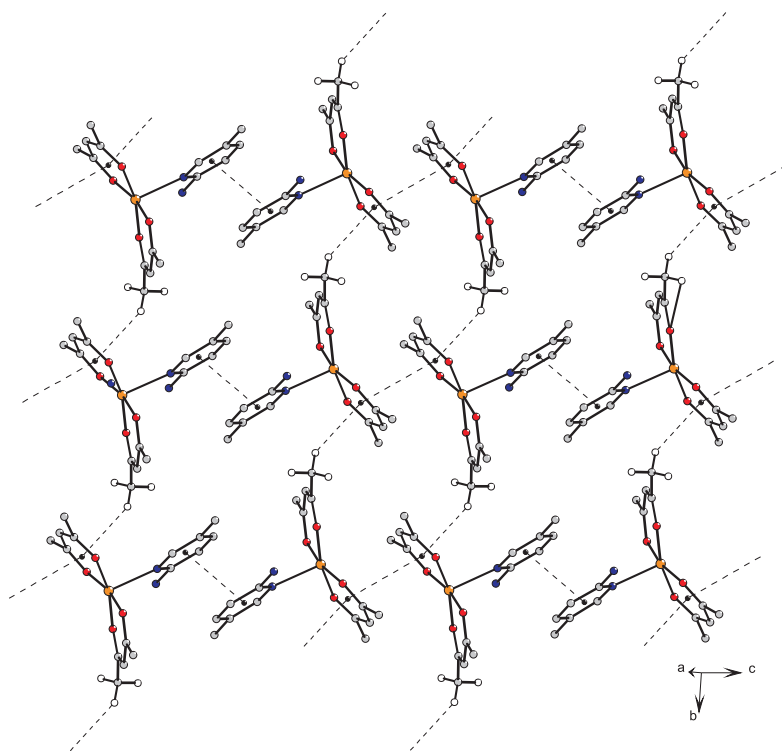


Figure 5.   Crystal packing in **2**. Dashed lines indicate π–π and C1–H1C · · · *Cg*1 interactions. For clarity, only hydrogen atoms on C1 are shown.
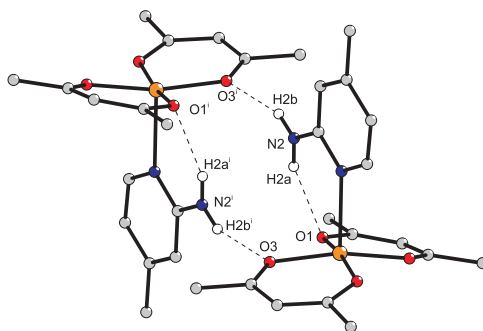
Figure 6. A hydrogen-bonded dimer in **3**. Dashed lines indicate hydrogen bonds. For clarity, hydrogen atoms not involved in the motif shown have been omitted. Symmetry code: (i) $1 - x, 2 - y, 2 - z$.

### 3.4. *Crystal aggregation of 3*

The crystal structure of **3** differs significantly from **1** and **2**, as expected from cell parameters. The presence of a methyl substituent on position 4 in 2,4-ampy does not prevent intermolecular N–H$\cdots$O hydrogen-bonding. Contrary to **1** and **2**, crystal structure of **3** contains centrosymmetric hydrogen-bonded dimers facilitated by N2–H2B$\cdots$O3 $(1 - x, 2 - y, 2 - z)$ interactions with the graph-set motif $R_2^2(12)$ (figure 6). This interaction is responsible for larger rotation of pyridine ring toward O1 as indicated by O1–Cu1–N1–C11 and O3–Cu1–N1–C11 torsion angles of $23.68(19)°$ and $-62.61(18)°$, respectively, compared to torsion angles observed in **1** and **2**. Hydrogen-bonded dimers aggregate into chains by strong $\pi$–$\pi$ interactions between two parallel neighboring Cu1–O3–C7–C8–C9–O4 chelate rings with a $Cg1\cdots Cg1$ $(1 - x, 1 - y, 2 - z)$ centroid–centroid distance of $3.4193(11)$ Å, a perpendicular distance from the centroid $Cg1$ to the plane of the other ring of $3.3983(8)$ Å and a centroid offset of $0.379$ Å (figure 7). Distance between the copper and C8 of the neighboring molecule Cu1$\cdots$C8 $(1 - x, 1 - y, 2 - z)$ is $3.413(2)$ Å. Additional feature found is that, contrary to interactions observed in **1** and **2**, pyridine ring in **3** is not involved in $\pi$–$\pi$ interactions and also no further aggregations are present.

### 4. Conclusion

Three copper(II) bis(pentane-2,4-dionato-$\kappa^2 O,O'$) compounds with methyl substituted 2-aminopyridines were prepared by the reaction of bis(pentane-2,4-dionato-$\kappa^2 O,O'$)copper(II) with selected methyl substituted 2-aminopyridines. Although the molecular structures are similar, distinctly different crystal aggregation was observed with infinite (**2**) or dimeric (**3**) intermolecular N–H$\cdots$O hydrogen-bonding depending on the position of a methyl substituent on the pyridine ring. Extended 3-D aggregation was found in **2**, but only chain formation in **1** and **3**. Such cases are valuable examples that can help to understand the non-covalent factors governing the supramolecular aggregation important for crystal engineering and crystal structure prediction.
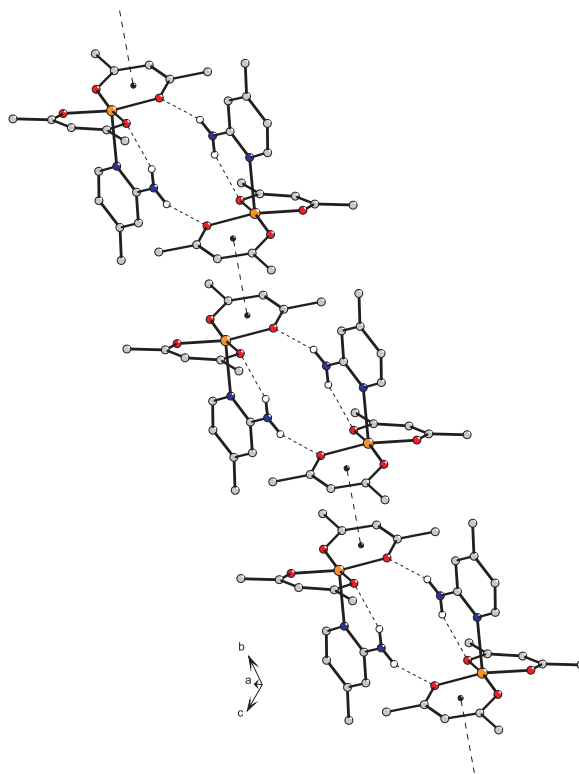
*F. Perdih*



Figure 7.  Chain formation in **3**. Dashed lines indicate hydrogen bonds and $\pi$–$\pi$ interactions. For clarity, hydrogen atoms not involved in the motif shown have been omitted.

## Supplementary material

CCDC 856963 (**2**), 856964 (**1**), 856965 (**3**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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