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# Synthesis, Supramolecular Structural Investigations of Co(II) and $\mathrm{Cu}(\mathrm{II})$ Azido Complexes with Pyridine-Type Ligands 

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#### Abstract

Two new $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$ azido complexes with 4-picoline (4-Pic) and pyridine-2carboxaldoxime (HAld) were synthesized by self-assembly of the organic ligand and the M (II) nitrate in the presence of azide as a co-ligand. Their structures were determined to be $[\mathrm{Co}(4-$ Pic $\left.)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{N}_{3}\right)\right] \mathrm{NO}_{3}{ }^{*} \mathrm{H}_{2} \mathrm{O}^{*} 4$-Pic (1) and $\left[\mathrm{Cu}(\mathrm{HAld})(\mathrm{Ald})\left(\mathrm{N}_{3}\right)\right]$ (2) using X-ray single crystal diffraction. In complex 1, the coordination geometry is a slightly distorted octahedron with a water molecule and azide ion located trans to one another. On the other hand, complex 2 has a distorted square pyramid $\mathrm{CuN}_{5}$ coordination sphere with N -atoms of the organic ligand as a basal plane and azide ion as apical. All types of intermolecular contacts and their contributions in the molecular packing were analyzed using Hirshfeld analysis. The intermolecular contacts, H ... H (53.9\%), O ... H (14.1\%), $\mathrm{N} \ldots \mathrm{H}(11.0 \%)$ and $\mathrm{H} \ldots \mathrm{C}(18.8 \%)$ in 1 , and $\mathrm{H} \ldots \mathrm{H}(27.4 \%), \mathrm{N} \ldots \mathrm{H}(27.7 \%), \mathrm{O} \ldots \mathrm{H}(14.7 \%)$ and $\mathrm{H} \ldots \mathrm{C}(13.6 \%)$ in 2 have the largest contributions. Of all the contacts, the $\mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{C} \ldots \mathrm{C}$ interactions in $\mathbf{2}$ and the $\mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{H} \ldots \mathrm{C}$ in $\mathbf{1}$ are apparently shorter than the van der Waals radii sum of the interacting atoms. Atoms in molecules (AIM) topological parameters explained the lower symmetry of the coordinated azide in $\mathbf{1}$ than $\mathbf{2}$.


Keywords: $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$ azido complexes; Hirshfeld analysis; atoms in molecules; X-ray single crystal structure; 4-picoline; pyridine-2-carboxaldoxime; intermolecular interactions

## 1. Introduction

Metal complexes have attracted the attention of researchers for their diverse and fascinating applications in different fields [1-6]. These compounds have interesting applications such as gas storage and separation of ions $[7,8]$. On the other hand, the coordination environment in metal complexes depends on many factors such as the nature of the metal ion, ligand and medium used $[9,10]$. Moreover, the presence of linker group such as azide has a great impact not only on the dimensionality of the resulting coordination compound but also on their functionality and applications [11-21].

The chemistry of azide containing compounds has attracted the attention of scientist due to the versatile applications of these compounds especially in the field of explosives. Some metal azides such as $\mathrm{Pb}\left(\mathrm{N}_{3}\right)_{2}$ and $\mathrm{Cu}\left(\mathrm{N}_{3}\right)_{2}$ are well known explosives [22,23]. Moreover, azide compounds are important as propellants in air bags [24]. Hence, these compounds could be considered as a good source of energy. Intuitively, the increase in $\mathrm{N}_{3}{ }^{-}$ion content in a compound has a vital role in obtaining better energy sources. Moreover, the azide binding mode in metal complexes is an important factor in achieving this purpose. Many azide binding modes have been reported in the literature, ranging from
ionic, terminal and $\mu-1,1$ (end-on) to $\mu-1,3$ (end-to-end) bridging modes. The azide binding modes depend on a number of factors including the type and oxidation state of the metal ion and the nature of the auxiliary ligand. Moreover, these factors have an important role in upholding the stability of the azide containing compounds. Cobalt azide complexes are generally stable compounds [25-27]. As a result, these azide complexes could be considered as promising compounds for tunable heat energy release. Based on the literature, the $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{~N}_{3}\right)\right]\left(\mathrm{N}_{3}\right)_{2}$ complex is the first well known azide complex [28].

On the other hand, nitrogen heterocycles such as pyridine compounds have great importance as ligands in coordination chemistry [29-31]. The introduction of the substituent has a pivotal role in changing the electronic, steric and conformational characteristics of the ligand which affect the ligand coordination ability [32-39]. In light of the fascinating structure and applications of azido complexes [40-42] with various N-heterocycles, our plan in the current work is to synthesize the $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$ azido complexes of 4-picoline (4-Pic) and pyridine-2-carboxaldoxime (HAld) (Figure 1). Combined experimental and theoretical studies were used to shed light on their structural aspects. In this regard, the structures obtained from the single crystal X-ray diffraction analyses were studied using Hirshfeld and DFT calculations.


4-Pic


Figure 1. Structure of 4-picoline (4-Pic) and pyridine-2-carboxaldoxime (HAld).

## 2. Experiment

### 2.1. Physicochemical Characterizations

All details regarding chemicals and physicochemical characterizations are given in Supplementary data.

### 2.2. Synthesis of the Metal Complexes $\mathbf{1}$ and $\mathbf{2}$

### 2.2.1. Synthesis of $\left.[\mathrm{Co}(4-\mathrm{Pic}))_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{N}_{3}\right)\right] \mathrm{NO}_{3}{ }^{*} \mathrm{H}_{2} \mathrm{O}^{*} 4$-Pic; $\mathbf{1}$

A solution of $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.2 \mathrm{mmole}$ in 10 mL ethanol) was added to 10 mL ethanolic solution of 1.0 mmole 4 -picoline ( $4-\mathrm{Pic}$ ), then 1 mL saturated aqueous solution of $\mathrm{NaN}_{3}$ was added dropwise with constant stirring for 10 min followed by filtration and the clear filtrate was left to slowly evaporate at rt. After one week, pink crystals of 1 were obtained.
$\left[\mathrm{Co}(4-\mathrm{Pic})_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{N}_{3}\right)\right] \mathrm{NO}_{3}{ }^{*} \mathrm{H}_{2} \mathrm{O}^{*} 4$-Pic; 1: Yield: 65\%; Anal. Calcd. $\mathrm{C}_{30} \mathrm{H}_{39} \mathrm{CoN}_{9} \mathrm{O}_{5}$ : C, $54.21 ; \mathrm{H}, 5.91 ;$ N, 18.97 ; Co, $8.87 \%$. Found: C, 54.09 ; H, $5.84 ;$ N, 18.83 ; Co, $8.96 \%$.

### 2.2.2. Synthesis of $\left[\mathrm{Cu}(\mathrm{HAld})(\mathrm{Ald})\left(\mathrm{N}_{3}\right)\right] ; 2$

A solution of $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}(0.2$ mmole in 10 mL ethanol) was added to 10 mL ethanolic solution of 0.4 mmole pyridine-2-aldoxime (HAld), then 1 mL saturated aqueous solution of $\mathrm{NaN}_{3}$ was added dropwise with constant stirring for 10 min followed by filtration and the clear filtrate was left to slowly evaporate at rt. After 5 days, dark green crystals of 2 were obtained.
[Cu(HAld)(Ald)( $\mathrm{N}_{3}$ )]; 2: Yield: 69\%; Anal. Calcd. $\mathrm{C}_{12} \mathrm{H}_{11} \mathrm{CuN}_{7} \mathrm{O}_{2}$ : C, 41.32; H, 3.18; N, 28.11; Cu, 18.22\%. Found: C, 41.21; H, 3.11; N, 27.97; Cu, 18.10\%.

### 2.3. X-ray Diffraction Analysis

The crystal structures of the two azide complexes were determined as described in the Supplementary Materials [43,44]. Crystal data are given in Table 1. It is worth noting that the crystals of complex 1 were extremely brittle and tended to decompose after a while on the diffractometer. The measurement was stopped before it was completed-due to crystal decomposition. Upon cooling, the material crumbled, ending up in a more or less polycrystalline lump. Thus, we decided to use the data measured at the best crystal in the sample and solve the structure based upon these data. Anyway even with the reduced dataset it was possible to determine the structure properly, without any deviations from the ideal shape of the displacement parameters or unusual interatomic distances.

Table 1. Crystal data of $\mathbf{1}$ and 2.

| Compound | 1 | 2 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{30} \mathrm{H}_{39} \mathrm{CoN}_{9} \mathrm{O}_{5}$ | $\mathrm{C}_{12} \mathrm{H}_{11} \mathrm{CuN}_{7} \mathrm{O}_{2}$ |
| Fw | 664.63 | 348.82 |
| T (K) | 293(2) K | 100(2) K |
| $\lambda(\AA)$ | 0.71073 A | 0.71073 A |
| cryst syst | Monoclinic | Monoclinic |
| Space group | $P 2_{1} / \mathrm{c}$ | $P 2_{1} / n$ |
| $a(\mathrm{~A})$ | 11.3305(7) | 6.8277(2) |
| $b(\AA)$ | 11.3887(15) | 10.2203(2) |
| $c(\AA)$ | 25.9243(16) | 18.8056(6) |
| $\beta\left({ }^{\circ}\right.$ ) | 101.672(2) | 94.700(2) |
| $V\left(\AA^{3}\right)$ | 3276.1(5) | 1307.86(6) |
| Z | 4 | 4 |
| $\rho_{\text {calc }}\left(\mathrm{Mg} / \mathrm{m}^{3}\right)$ | $1.347 \mathrm{Mg} / \mathrm{m}^{3}$ | $1.772 \mathrm{Mg} / \mathrm{m}^{3}$ |
| $\mu\left(\mathrm{Mo} \mathrm{K} \alpha\right.$ ) $\left(\mathrm{mm}^{-1}\right)$ | $0.576 \mathrm{~mm}^{-1}$ | $1.690 \mathrm{~mm}^{-1}$ |
| F(000) | 1396 | 708 |
| $\theta$-range | 2.180 to $26.341^{\circ}$ | 2.173 to $32.498^{\circ}$ |
| No. reflns. | 7685 | 28,102 |
| Unique reflns. | 4249 [ $R(\mathrm{int}$ ) $=0.0414]$ | $4745[R(\mathrm{int})=0.0310]$ |
| Completeness to theta $=25.242^{\circ}$ | 64.10\% | 100.00\% |
| $\operatorname{GOOF}\left(F^{2}\right)$ | 1.037 | 1.032 |
| Final $R$ indices [ $\mathrm{I}>2$ sigma(I)] | $R_{1}=0.0392, w R_{2}=0.0930$ | $R_{1}=0.0229, w R_{2}=0.0635$ |
| R indices (all data) | $R_{1}=0.0754, w R_{2}=0.1144$ | $R_{1}=0.0264, w R_{2}=0.0657$ |
| CCDC | 2,158,205 | 2,158,206 |

## 3. Hirshfeld and DFT Calculations

The topology analyses including Hirshfeld calculations, construction of the different maps ( $\mathrm{d}_{\text {norm }}$, shape index (SI) and curvedness) and decomposition of the different intermolecular contacts were performed using Crystal Explorer 17.5 program [45-47]. DFT computational details are described in the Supplementary Materials [48-52].

## 4. Results and Discussion

### 4.1. X-ray Structure Description

### 4.1.1. Structure of $\left[\mathrm{Co}(4-\mathrm{Pic})_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{N}_{3}\right)\right] \mathrm{NO}_{3}{ }^{*} \mathrm{H}_{2} \mathrm{O}^{*} 4$-Pic; $\mathbf{1}$

This Co (II) complex crystallizes in the monoclinic crystal system and space group $\mathrm{P} 2_{1} / \mathrm{c}$. The unit cell parameters are $\mathrm{a}=11.3305(7) \AA, \mathrm{b}=11.3887(15) \AA \mathrm{c}=25.9243(16) \AA$ and $\beta=101.672(2)^{\circ}, 101.672(2)^{\circ}, \mathrm{V}=3276.1(5) \mathrm{A}^{3}, \mathrm{Z}=4$. Compound $\mathbf{1}$ is a cationic complex in which the coordination sphere comprises a hexa-coordinated $\mathrm{Co}(\mathrm{II})$ ion (Figure 2). There are four $\mathrm{Co}-\mathrm{N}$ interactions with the four 4 -Pic ligand units as N -donor ligand via the heterocyclic nitrogen of the pyridine moiety. The Co-N lengths vary from 2.160(4) $\AA$ (Co1$\mathrm{N} 4)$ to $2.211(3) \AA(\mathrm{Co} 1-\mathrm{N} 5)$. The angles of the trans bonds N4-Co1-N6 and N5-Co1-N7 are $178.48(10)^{\circ}$ and $175.25(10)^{\circ}$, respectively, while the angles of the cis $\mathrm{N}-\mathrm{Co}-\mathrm{N}$ bonds range from $87.04(14)^{\circ}(\mathrm{N} 6-\mathrm{Co} 1-\mathrm{N} 7)$ to $93.06(13)^{\circ}(\mathrm{N} 4-\mathrm{Co} 1-\mathrm{N} 5)$. The coordination sphere of the

Co (II) is completed by a terminally coordinated azide ion and a water molecule located trans to one another. The corresponding Co1-N1 and Co1-O1 bond lengths are 2.102(3) and $2.091(2) \AA$, respectively, while the O1-Co1-N1 is $178.79(16)^{\circ}$ which is very close to the ideal value of $180^{\circ}$ (Table 2). Hence the $\mathrm{CoN}_{5} \mathrm{O}$ coordination geometry is a slightly distorted octahedron. The outer sphere of 1 contains one nearby nitrate anion and two neutral molecules, which are the crystal water and a fifth free 4-Pic molecule.


Figure 2. X-ray structure of 1 drawn at $50 \%$ probability level for thermal ellipsoids. The labels of the aromatic and aliphatic protons are not depicted for better clarity.

Table 2. Bond lengths ( $\AA$ ) and angles $\left(^{\circ}\right.$ ) of complex 1.

| Bond | Bond Length | Bond | Bond Length |
| :---: | :---: | :---: | :---: |
| $\operatorname{Co}(1)-\mathrm{O}(1)$ | $2.091(2)$ | $\mathrm{Co}(1)-\mathrm{N}(6)$ | $2.181(4)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $2.102(3)$ | $\mathrm{Co}(1)-\mathrm{N}(7)$ | $2.198(3)$ |
| $\mathrm{Co}(1)-\mathrm{N}(4)$ | $2.160(4)$ | $\mathrm{Co}(1)-\mathrm{N}(5)$ | $2.211(3)$ |
| Bonds | Angle | Bonds | Angle |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $178.79(16)$ | $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(7)$ | $89.77(11)$ |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(4)$ | $88.80(12)$ | $\mathrm{N}(4)-\mathrm{Co}(1)-\mathrm{N}(7)$ | $91.54(14)$ |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(4)$ | $90.50(15)$ | $\mathrm{N}(6)-\mathrm{Co}(1)-\mathrm{N}(7)$ | $87.04(14)$ |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(6)$ | $91.72(12)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(5)$ | $89.67(9)$ |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(6)$ | $88.96(15)$ | $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(5)$ | $91.35(11)$ |
| $\mathrm{N}(4)-\mathrm{Co}(1)-\mathrm{N}(6)$ | $178.48(10)$ | $\mathrm{N}(4)-\mathrm{Co}(1)-\mathrm{N}(5)$ | $93.06(13)$ |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(7)$ | $89.27(9)$ | $\mathrm{N}(6)-\mathrm{Co}(1)-\mathrm{N}(5)$ | $88.37(14)$ |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(7)$ | $175.25(10)$ |  |  |

The structure of complex $\mathbf{1}$ comprised numerous intra- and intermolecular hydrogen bonding interactions. Presentation of these hydrogen bond contacts is shown in Figure 3 while the hydrogen bond parameters are depicted in Table 3. It is clear that the nitrate counter anion in the outer sphere acts as a hydrogen bond acceptor which connects the crystal water and free 4-Pic molecules with the complex cationic part via the coordinated water as hydrogen bond donor. Moreover, the latter form a short and strong O1-H2A ... O 2 hydrogen bond with the crystal water as hydrogen bond acceptor. It is worth noting
that there is no significant direct interaction between the complex cationic unit and the free 4 -Pic molecule.


Figure 3. H-bridge contacts (A) and H-bonding network (B) in 1.

Table 3. Hydrogen bonds in complex 1.

| D-H... A | d(D-H) | d(H... A) | <DHA | $\mathrm{d}(\mathrm{D} \ldots \mathrm{A})$ | Symmetry Code |
| :---: | :---: | :---: | :---: | :---: | :---: |
| O1-H1A ... O3 | 0.853 | 2.568 | 133.64 | 3.216 |  |
| O1-H1A ... O4 | 0.853 | 1.909 | 170.04 | 2.753 |  |
| O1-H2A ... O2 | 0.807 | 1.859 | 178.01 | 2.665 | [ $\mathrm{x}+1, \mathrm{y}, \mathrm{z}]$ |
| O2-H3A ... N8 | 0.819 | 1.973 | 173.17 | 2.788 |  |
| O2-H4A ... O3 | 0.866 | 1.953 | 167.15 | 2.803 | [ $-\mathrm{x}+1, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2]$ |
| O2-H4A ... O5 | 0.866 | 2.611 | 135.83 | 3.288 | $[-x+1, y-1 / 2,-z+1 / 2]$ |
| C7-H7 . . . N1 | 0.93 | 2.483 | 124.23 | 3.103 |  |
| C10-H10 . . O 5 | 0.93 | 2.513 | 139.78 | 3.278 | $[-x+1, y-1 / 2,-z+1 / 2]$ |
| C11-H11 ... O1 | 0.93 | 2.496 | 121.54 | 3.086 |  |
| C17-H17 . . . N1 | 0.93 | 2.468 | 120.95 | 3.052 |  |
| C25-H25 ... O3 | 0.93 | 2.658 | 158.25 | 3.538 | [ $\mathrm{x}-1, \mathrm{y}, \mathrm{z}$ ] |
| C28-H28 ... O4 | 0.93 | 2.584 | 168.86 | 3.501 |  |
| C29-H29 . . O O | 0.93 | 2.586 | 139.48 | 3.348 | $[-x+1, y-1 / 2,-z+1 / 2]$ |

As shown in Figure 4, there is an alternating arrangement for the inner and outer spheres of the complex. In this packing structure the complex cationic units form nearly parallel layers along the $b c$ plane, while a second layer of the crystal water, nitrate anion and the free 4 -Pic molecule interpenetrate the layers of the cationic complex. The two layer structures are held together via a complicated set of weak and strong H ... O bridges.

### 4.1.2. Structure of $\left[\mathrm{Cu}(\mathrm{HAld})(\right.$ Ald $\left.)\left(\mathrm{N}_{3}\right)\right] ; 2$

This $\mathrm{Cu}(\mathrm{II})$ complex crystallizes in the monoclinic crystal system and space group $\mathrm{P} 2_{1} / \mathrm{n}$. The unit cell parameters are $\mathrm{a}=6.8277(2) \AA, \mathrm{b}=10.2203(2) \AA, \mathrm{c}=18.8056(6) \AA$ and $94.700(2)^{\circ}, \mathrm{V}=1307.86(6) \mathrm{A}^{3}, \mathrm{Z}=4$. Compound 2 is a neutral complex in which the $\mathrm{Cu}(\mathrm{II})$ is penta-coordinated with the two HAld/Ald ${ }^{-}$organic ligand combination as bidentate $N N$-chelate, in addition to one terminally coordinated azide ion (Figure 5). In this structure, the HAld/Ald ${ }^{-}$organic ligand combination represents one deprotonated mononegative (Ald ${ }^{-}$) and one neutral (HAld) unit. Hence, the X-ray structure of this complex comprised electrically neutral monomers of the $\left[\mathbf{C u}(\mathbf{H A l d})(\mathbf{A l d})\left(\mathbf{N}_{3}\right)\right]$ complex. Selected bond lengths and angles for the coordination sphere are depicted in Table 4. The Cu-N(pyridine) lengths are generally longer than the $\mathrm{Cu}-\mathrm{N}$ (oxime) in both ligand units. The Cu1-N1 (2.0341(9) Å) and Cu1-N2 $(1.9967(9) \AA)$ bonds in one unit are slightly longer than the corresponding Cu1-N3 (2.0480(9) Å) and Cu1-N4 (1.9946(9) $\AA)$ bonds in the other ligand unit. The last $\mathrm{Cu} 1-\mathrm{N} 5$ interaction with the azide ligand is the longest (2.2158(10) $\AA$ ). Hence the structure of the coordination sphere is more like a distorted square pyramid where the N -atoms from the organic ligand units represent the base of the square while the N5 atom from the azide anion acts as apical. Based on Addison criterion [53], the largest angles N4-Cu1-N1
( $\beta=170.83^{\circ}$ ) and N2-Cu1-N3 $\left(\alpha=156.74^{\circ}\right)$ give a $\tau=\frac{(\beta-\alpha)}{60}$ value of 0.24 suggesting as a distorted square pyramid $\mathrm{CuN}_{5}$ coordination environment.


Figure 4. Packing scheme of compound 1. The projections along [100] (A) and [010] (B) directions, respectively. Hydrogen atoms are omitted in both projections.


Figure 5. X-ray structure of 2 drawn at $50 \%$ probability level for thermal ellipsoids. The labels of the protons, except split H 1 and H 2 atoms are not depicted for better clarity.

Table 4. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for complex 2.

| Bond | Bond Length | Bond | Bond length |
| :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1)-\mathrm{N}(4)$ | $1.9946(9)$ | $\mathrm{Cu}(1)-\mathrm{N}(3)$ | $2.0480(9)$ |
| $\mathrm{Cu}(1)-\mathrm{N}(2)$ | $1.9967(9)$ | $\mathrm{Cu}(1)-\mathrm{N}(5)$ | $2.2158(10)$ |
| $\mathrm{Cu}(1)-\mathrm{N}(1)$ | $2.0341(9)$ |  |  |
| Bonds | Angle | Bonds | Angle |
| $\mathrm{N}(4)-\mathrm{Cu}(1)-\mathrm{N}(2)$ | $90.94(4)$ | $\mathrm{N}(1)-\mathrm{Cu}(1)-\mathrm{N}(3)$ | $106.57(4)$ |
| $\mathrm{N}(4)-\mathrm{Cu}(1)-\mathrm{N}(1)$ | $170.83(4)$ | $\mathrm{N}(4)-\mathrm{Cu}(1)-\mathrm{N}(5)$ | $90.34(4)$ |
| $\mathrm{N}(2)-\mathrm{Cu}(1)-\mathrm{N}(1)$ | $80.57(4)$ | $\mathrm{N}(2)-\mathrm{Cu}(1)-\mathrm{N}(5)$ | $101.56(4)$ |
| $\mathrm{N}(4)-\mathrm{Cu}(1)-\mathrm{N}(3)$ | $79.98(4)$ | $\mathrm{N}(1)-\mathrm{Cu}(1)-\mathrm{N}(5)$ | $94.74(4)$ |
| $\mathrm{N}(2)-\mathrm{Cu}(1)-\mathrm{N}(3)$ | $156.74(4)$ | $\mathrm{N}(3)-\mathrm{Cu}(1)-\mathrm{N}(5)$ | $99.88(4)$ |

The analysis of the residual electron densities in the region of the oxygen atoms of the oxime ligands showed two approximately equal peaks for the protons of the N-O-H group. Therefore, a split position for this proton was added, the H1 and H2 positions. It is obvious that the neutral protonated ligand (HAld) and the deprotonated anion (Ald) ${ }^{-}$ are statistically distributed 50:50 to the respective position. The fact that the displacement
ellipsoids are more or less round leads to the assumption that this disorder has hardly any influence on the crystal structure and the interatomic distances and bond angles.

As can be seen from Figure 5, the two organic ligand units are located syn to one another and found stabilized by the intramolecular O-H . . . O hydrogen bridge shown as a turquoise dotted line in Figure 6A. In addition, the structure of 2 showed some intermolecular $\mathrm{O} \ldots \mathrm{H}$ and $\mathrm{N} \ldots \mathrm{H}$ hydrogen bridge contacts which connect the complex molecules to build the 3D supramolecular structure of this complex (Table 5). In this complex, all the intermolecular contacts belong to the weak C-H ... O and C-H ... N interactions where the oxime oxygen and the azide nitrogen are the hydrogen bond acceptor sites while the aromatic $\mathrm{C}-\mathrm{H}$ bonds are the hydrogen bond donors. Presentation of the packing scheme along the $a$-axis is shown in Figure 6B.


Figure 6. Hydrogen bridge contacts (A) and packing view along a-axis (B) in 2.

Table 5. Hydrogen bonds in complex 2.

| D-H | d(D-H) | $\mathbf{d}(\mathbf{H} \ldots$ A) | <DHA | d(D $\ldots$ A) | Symmetry Code |
| :---: | :---: | :---: | :---: | :---: | :---: |
| O1-H1 ... O2 | $0.84(3)$ | $1.61(3)$ | $2.4431(13)$ | $174(4)$ |  |
| C3-H3 . . O2 | 0.95 | 2.54 | $3.3761(15)$ | 148 | $-1 / 2+\mathrm{x}, 3 / 2-\mathrm{y}, 1 / 2+\mathrm{z}$ |
| C7-H7 . . N7 | 0.95 | 2.57 | $3.3751(15)$ | 143 | $1-\mathrm{x}, 2-\mathrm{y},-\mathrm{z}$ |
| C9-H9 .. O1 | 0.95 | 2.35 | $3.2252(14)$ | 152 | $\mathrm{x}, 1+\mathrm{y}, \mathrm{z}$ |
| C10-H10 . . N5 | 0.95 | 2.54 | $3.2872(15)$ | 136 | $1 / 2-\mathrm{x}, 1 / 2+\mathrm{y}, 1 / 2-\mathrm{z}$ |
| C11-H11 . N7 | 0.95 | 2.51 | $3.2984(15)$ | 141 | $1-\mathrm{x}, 2-\mathrm{y},-\mathrm{z}$ |
| C12-H12 . . N6 | 0.95 | 2.62 | $3.4037(15)$ | 140 | $1 / 2-\mathrm{x},-1 / 2+\mathrm{y}, 1 / 2-\mathrm{z}$ |

An interesting feature of packing for the complex units in 2 is shown in Figure 7A. The molecules of complex 2 are connected via the C-H $\ldots$. N and C-H ... O interactions along the ac plane. The aromatic ring systems are nearly parallel to one another, leading to some $\pi-\pi$ stacking interactions which connect the complex units through the $a$-direction (Figure 7B). The shortest C . . C contacts are C2 . . C10 ( $3.383 \AA$ ) and C3 . . C8 ( $3.325 \AA$ ).


Figure 7. Packing scheme of 2 along the monoclinic $b$-axis (A) and $\pi-\pi$ stacking interactions extended through the $a$-direction (B). Hydrogen atoms are omitted in both projections.

### 4.2. Analysis of Molecular Packing

The results of the Hirshfeld calculations are important for accurately analyzing the molecular packing of crystalline compounds. Different maps such as $\mathrm{d}_{\text {norm }}$, shape index and curvedness are important for deciding the important contacts (Figures S1 and S2 (Supplementary Materials)). The fingerprint plot was used to quantitatively estimate the different intermolecular contacts affecting the packing of this complex in the crystal. The dominant contacts are the $\mathrm{H} \ldots \mathrm{H}(53.9 \%), \mathrm{O} \ldots \mathrm{H}(14.1 \%), \mathrm{N} \ldots \mathrm{H}(11.0 \%)$ and $\mathrm{H} \ldots \mathrm{C}$ (18.8\%) interactions (Figure 8). Not all these contacts showed the characteristics of strong interactions. The red spots in the $\mathrm{d}_{\text {norm }}$ map are related to the short distance $\mathrm{O} \ldots \mathrm{H}$, $\mathrm{N} \ldots \mathrm{H}$ and $\mathrm{H} \ldots \mathrm{C}$ contacts. Moreover, the fingerprint plots of these contacts showed the characteristic spikes of strong intermolecular interactions (Figure 8).

There is extensive number of the polar $\mathrm{O} \ldots \mathrm{H}$ interactions which are shorter than the vdWs radii sum of the O and H atoms. Moreover, some significantly short $\mathrm{N} \ldots \mathrm{H}$ and H ... C interactions were detected. List of the short contacts and the corresponding interaction distances are depicted in Table 6. The shortest interaction distances are 2.445, 2.676 and $1.682 \AA$, corresponding to $\mathrm{N} 9 \ldots$ H1A, H3A ... C25 and O2 . . H2A contacts, respectively.

In the neutral $\mathrm{Cu}(\mathrm{II})$ complex 2 , the crystal stability is controlled by a large number of intermolecular contacts such as the $\mathrm{H} \ldots \mathrm{H}(27.4 \%), \mathrm{N} \ldots \mathrm{H}(27.7 \%), \mathrm{O} \ldots \mathrm{H}(14.7 \%)$, H ... C (13.6\%) which are considered the most dominant contacts in the crystal packing (Figure 9). Only the $\mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{C} \ldots \mathrm{C}$ interactions appeared as red regions in the $\mathrm{d}_{\text {norm }}$ map, indicating that these contacts are shorter than the vdW radii sum of the interacting atoms (Table 6). The N7 ... H11, O2 ... H3 and C3 ... C8 interactions are the shortest and the corresponding interaction distances are 2.406, 2.424 and $3.325 \AA$, respectively. Moreover, the SI map showed the characteristic red/blue triangles for the $\pi-\pi$ interactions (Figure 9).


Figure 8. Hirshfeld surfaces and pie chart showing the intermolecular interactions in 1. A-C in the $d_{\text {norm }}$ map belong to the $\mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{H} \ldots \mathrm{C}$ contacts, respectively.

Table 6. Short distance contacts in compounds $\mathbf{1}$ and 2.

| Contact | Distance | Contact | Distance | Contact | Distance |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 |  |  | 2 |  |
| N3 . . . H24B | 2.498 | O3 . . H25 | 2.517 | C3 . . . C8 | 3.325 |
| N3 ... H4 | 2.591 | O2 ... H2A | 1.682 | N7 . . H7 | 2.461 |
| N9 ... H1A | 2.445 | O3 ... H4A | 1.839 | N7 . . H11 | 2.406 |
| H13 ... C25 | 2.684 | O5 ... H4A | 2.529 | N7 . . . H2B | 2.521 |
| H3A . . C25 | 2.676 | O5 ... H12C | 2.513 | N6 . . . H12 | 2.519 |
| H20 ... C9 | 2.749 | O5 . . . H10 | 2.397 | N5 ... H10 | 2.442 |
| O4... H1A | 1.781 | O5 . . . H29 | 2.472 | O2 . . H3 | 2.424 |
| O3 ... H1A | 2.482 | $\mathrm{O} 4 \ldots \mathrm{H} 28$ | 2.453 | $\mathrm{O} 2 \ldots . \mathrm{H} 4$ | 2.531 |
|  |  |  |  | O1 . . . H9 | 2.236 |

### 4.3. AIM Studies

The free $\mathrm{N}_{3}{ }^{-}$ion is symmetric as the two $\mathrm{N}-\mathrm{N}$ bonds are equidistant. In contrast, the coordinated azide is asymmetric and the two $\mathrm{N}-\mathrm{N}$ bonds are not equivalent [54,55]. In this regard, the atoms in molecules (AIM) calculations [51,56-61] were used to judge this behavior in the studied $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$ complexes. The calculated AIM topological parameters of the $\mathrm{N}-\mathrm{N}$ bonds are presented in Table 7. From the first glance, the two N-N bonds of the coordinated azide are not equivalent. The difference in the $\mathrm{N}-\mathrm{N}$ distances are 0.04 and $0.02 \AA$ in complexes 1 and 2 , respectively where the NA-NB bonds are generally longer than the NB-NC ones (Figure 10). Hence, the formation of the metal azide bond affects its symmetry.


Figure 9. Hirshfeld surfaces and pie chart showing the intermolecular interactions in 2. A-C in the $\mathrm{d}_{\text {norm }}$ map belong to the $\mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{C} \ldots \mathrm{C}$ contacts, respectively.

Table 7. The topological parameters of the azide N-N bonds.

| Bond | $\mathbf{d}_{\mathrm{N}-\mathrm{N}}$ | $\Delta \mathrm{d}$ | $\rho(\mathbf{r}), \mathbf{a . u}$ | $\nabla^{\mathbf{2}} \boldsymbol{\rho ( \mathbf { r } ) ^ { \mathbf { a } }}$ | $\mathbf{V}(\mathbf{r}) / \mathbf{G}(\mathbf{r})^{\mathbf{b}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Complex $\mathbf{1}$ |  |  |  |  |  |
| NA-NB | $1.189(6)$ | 0.04 | 0.4847 | -1.3846 | 2.884 |
| NB-NC | $1.149(7)$ |  | 0.5424 | -1.4216 | 2.670 |
| Complex 2 |  |  |  |  |  |
| NA-NB | $1.192(1)$ | 0.02 | 0.4833 | -1.2346 | 2.743 |
| NB-NC | $1.172(1)$ |  | 0.5105 | -1.2270 | 2.623 |

${ }^{\text {a }}$ Laplacian of electron density; ${ }^{\mathrm{b}}$ Ratio of potential to kinetic energy density.



Figure 10. The resonance structures of the terminally coordinated azide.
The electron density $(\rho(r))$ at the bond critical point was used as a measure for the bond strength. The $\rho(\mathrm{r})$ values of the NA-NB bonds are calculated to be 0.4847 and 0.4833 a.u. in complexes $\mathbf{1}$ and 2, respectively. The corresponding values for the NB-NC bonds are 0.5424 and 0.5105 a.u., respectively. These results are in agreement with the NA-NB bonds longer than the NB-NC ones in both complexes. Moreover, the results indicated that the degree of asymmetry is higher in the case of complex 1 than 2 . On the other hand, the $\rho(\mathrm{r})$ values at the N-N BCPs are higher than $0.1 \mathrm{a} . \mathrm{u}$. and the $\nabla^{2} \rho(\mathrm{r})$ values are negative, indicating clear covalent interactions (Table 7).

Another application of the AIM parameters is to identify the nature and strength of the different $\mathrm{M}-\mathrm{N}$ and $\mathrm{M}-\mathrm{O}$ bonds in the studied systems (Table 8). The low electron density $(\rho(\mathrm{r})<0.10 \mathrm{au})$ values and positive $\mathrm{H}(\mathrm{r})$ as well as the positive $\nabla^{2} \rho(\mathrm{r})$ and $\mathrm{V}(\mathrm{r}) / \mathrm{G}(\mathrm{r})<1$ for the $\mathrm{Co}-\mathrm{N}$ bonds with the organic ligand indicated mainly closed shell coordination interactions [62-65]. The same is true for the Co-O bond with the coordinated water
molecule. The Co-N(azide) bond has more negative $\mathrm{H}(\mathrm{r})$ and slightly higher $\mathrm{V}(\mathrm{r}) / \mathrm{G}(\mathrm{r})$ than the $\mathrm{Co}-\mathrm{N}(4-\mathrm{Pic})$. The slightly negative $\mathrm{H}(\mathrm{r})$ and $\mathrm{V}(\mathrm{r}) / \mathrm{G}(\mathrm{r})$ marginally higher than 1 for all $\mathrm{Cu}-\mathrm{N}$ bonds in 2 revealed very few covalent characters. On the other hand, the high $\rho(\mathrm{r})$ values are indicative on the bond strength. As can be seen from Table 8, shorter coordination interaction for a given bond has higher $\rho(\mathrm{r})$ values at the BCP than the longer one.

Table 8. The AIM parameters for compounds 1 and 2.

| Bond | Bond Length | $\rho(\mathbf{r}) ; \mathbf{a . u}$. | $\mathbf{H}(\mathbf{r})^{\mathbf{a}} ; \mathbf{a . u}$. | $\mathrm{V}(\mathbf{r}) / \mathrm{G}(\mathbf{r})^{\mathbf{b}}$ | $\nabla^{\mathbf{2}} \boldsymbol{\rho ( \mathbf { r } ) ^ { \mathbf { c } }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Complex $\mathbf{1}$ |  |  |  |  |  |
| Co1-O1 | $2.091(2)$ | 0.0401 | 0.0023 | 0.974 | 0.3519 |
| Co1-N1 | $2.102(3)$ | 0.0616 | -0.0088 | 1.104 | 0.3040 |
| Co1-N4 | $2.159(4)$ | 0.0419 | 0.0008 | 0.991 | 0.3589 |
| Co1-N5 | $2.211(3)$ | 0.0360 | 0.0017 | 0.975 | 0.2868 |
| Co1-N6 | $2.181(4)$ | 0.0396 | 0.0008 | 0.991 | 0.3380 |
| Co1-N7 | $2.197(3)$ | 0.0377 | 0.0013 | 0.982 | 0.2989 |
| Complex 1 |  |  |  |  |  |
| Cu1-N1 | $2.034(1)$ | 0.0553 | -0.0050 | 1.041 | 0.4637 |
| Cu1-N2 | $1.997(1)$ | 0.0588 | -0.0043 | 1.032 | 0.5258 |
| Cu1-N3 | $2.048(1)$ | 0.0552 | -0.0049 | 1.042 | 0.4513 |
| Cu1-N4 | $1.994(1)$ | 0.0798 | -0.0191 | 1.175 | 0.3597 |
| Cu1-N5 | $2.216(1)$ | 0.0381 | 0.0000 | 1.000 | 0.2947 |

${ }^{\text {a }}$ Total energy density; ${ }^{\text {b }}$ potential to kinetic energy density; ${ }^{\mathrm{c}}$ Laplacian of electron density.

### 4.4. Natural Charges

Decomposition of the charge distribution at the different ligand groups coordinated to the metal ion enabled us to assess the amount of electron density transferred from the ligand groups as Lewis base to the metal ion as Lewis acid. Natural charge calculations of complexes 1 and 2 were used to predict the amount of electron density transferred from the ligand groups to the donor atoms. A summary of natural charges at these fragments is presented in Table 9. The charges at the metal centers are +0.9623 and +0.7655 for complexes $\mathbf{1}$ and 2, respectively instead of +2 . Hence, there is 1.0377 e and 1.2345 e were transferred from the ligand groups to $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$, respectively. In case of the former, 0.5804 e was transferred from the four 4-Pic ligand units while the azide and water molecule transferred 0.2862 and 0.1278 , respectively. In the case of the latter, 0.3354 e was transferred from the neutral HAld while the anionic Ald ${ }^{-}$and azide ions transferred 0.6198 e and 0.2973 e to the $\mathrm{Cu}(\mathrm{II})$ site, respectively.

Table 9. The natural charges at metal center, ligand groups.

|  | $\mathbf{1}$ |  | $\mathbf{2}$ |
| :---: | :---: | :---: | :---: |
| Co | 0.9623 | Cu | 0.7655 |
| 4 -Pic | 0.5804 | HAld | 0.3354 |
| $\mathrm{H}_{2} \mathrm{O}$ | 0.1278 | Ald $^{-}$ | -0.7207 |
| $\mathrm{~N}_{3}{ }^{-}$ | -0.7138 | $\mathrm{~N}_{3}{ }^{-}$ | -0.7207 |
| $\mathrm{NO}_{3}{ }^{-}$ | -0.9567 |  |  |

## 5. Conclusions

The molecular and supramolecular structures of the monomeric complexes $[\mathrm{Co}(4-$ Pic $\left.)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{N}_{3}\right)\right] \mathrm{NO}_{3}{ }^{*} \mathrm{H}_{2} \mathrm{O}^{*} 4$-Pic (1) and $\left[\mathrm{Cu}(\mathrm{HAld})(\mathrm{Ald})\left(\mathrm{N}_{3}\right)\right]$ (2) were presented. In complex 1, the $\mathrm{CuN}_{5} \mathrm{O}$ coordination geometry is a slightly distorted octahedron while the CuN 5 coordination sphere in complex 2 has a square pyramidal configuration. In both complexes, the azide ion is terminally coordinated with the metal ion. For the organic ligands used in this work, the 4 -picoline (4-Pic) is a monodentate ligand in 1 while the pyridine-2-carboxaldoxime (HAld) is a bidentate chelate in 2 . The crystal packing is dominated by $\mathrm{H} \ldots \mathrm{H}, \mathrm{O} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}$ and $\mathrm{H} \ldots \mathrm{C}$ interactions in $\mathbf{1}$ based on Hirshfeld
analysis. For 2, the $\mathrm{H} \ldots \mathrm{H}, \mathrm{N} \ldots \mathrm{H}, \mathrm{O} \ldots \mathrm{H}$ and $\mathrm{H} \ldots \mathrm{C}$ are the most dominant contacts. The charges at the metal centers are calculated to be +0.9623 and +0.7655 for complexes 1 and 2. Moreover, AIM is used to identify the nature and strength of the $\mathrm{M}-\mathrm{N}$ and $\mathrm{M}-\mathrm{O}$ bonds. Selection of the prober organic ligand could have a great impact on extending the dimensionality of the metal complex. Hence, more functional ligands will be introduced in our future work for this task.

Supplementary Materials: The following supporting information can be downloaded at: https:/ / www.mdpi.com/article/10.3390/cryst13020346/s1, X-ray single crystal diffraction measurement; Computational details; Figure S1 Hirshfeld surfaces of 1. Figure S2 Hirshfeld surfaces of 2.

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