



Article Synthesis, Supramolecular Structural Investigations of Co(II) and Cu(II) Azido Complexes with Pyridine-Type Ligands

Mezna Saleh Altowyan ¹, Jörg H. Albering ², Assem Barakat ³, Saied M. Soliman ^{4,*} and Morsy A. M. Abu-Youssef ^{4,*}

- ¹ Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P.O. Box 84428, Riyadh 11671, Saudi Arabia
- ² Graz University of Technology, Mandellstr. 11/III, A-8010 Graz, Austria
- ³ Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
- ⁴ Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt
- * Correspondence: saeed.soliman@alexu.edu.eg (S.M.S.); morsy5@alexu.edu.eg (M.A.M.A.-Y.)

Abstract: Two new Co(II) and Cu(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 [Co(4-Pic)₄(H₂O)(N₃)]NO₃*H₂O*4-Pic (**1**) and [Cu(HAld)(Ald)(N₃)] (**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 CuN₅ 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%), N … H (11.0%) and H … C (18.8%) in **1**, and H … H (27.4%), N … H (27.7%), O … H (14.7%) and H … C (13.6%) in **2** have the largest contributions. Of all the contacts, the O … H, N … H and C … C interactions in **2** and the O … H, N … H and H … C in **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 **1** than **2**.

Keywords: Co(II) and Cu(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 $Pb(N_3)_2$ and $Cu(N_3)_2$ 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 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



Citation: Altowyan, M.S.; Albering, J.H.; Barakat, A.; Soliman, S.M.; Abu-Youssef, M.A.M. Synthesis, Supramolecular Structural Investigations of Co(II) and Cu(II) Azido Complexes with Pyridine-Type Ligands. *Crystals* **2023**, *13*, 346. https://doi.org/10.3390/ cryst13020346

Academic Editor: Alexander Y. Nazarenko

Received: 31 January 2023 Revised: 12 February 2023 Accepted: 15 February 2023 Published: 17 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). ionic, terminal and μ -1,1 (end-on) to μ -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 [Co(NH₃)₅(N₃)](N₃)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 Co(II) and Cu(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.



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 1 and 2

2.2.1. Synthesis of [Co(4-Pic)₄(H₂O)(N₃)]NO₃*H₂O*4-Pic; 1

A solution of $Co(NO_3)_2.6H_2O$ (0.2 mmole in 10 mL ethanol) was added to 10 mL ethanolic solution of 1.0 mmole 4-picoline (4-Pic), then 1 mL saturated aqueous solution of NaN₃ 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.

[Co(4-Pic)₄(H₂O)(N₃)]NO₃*H₂O*4-Pic; **1**: Yield: 65%; Anal. Calcd. C₃₀H₃₉CoN₉O₅: C, 54.21; 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 [Cu(HAld)(Ald)(N₃)]; 2

A solution of $Cu(NO_3)_2.3H_2O$ (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 NaN₃ 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)(N₃)]; **2**: Yield: 69%; Anal. Calcd. C₁₂H₁₁CuN₇O₂: 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 dat	a of 1 and 2
------------	-------------	----------------------------

Compound	1	2
Empirical formula	C ₃₀ H ₃₉ CoN ₉ O ₅	C ₁₂ H ₁₁ CuN ₇ O ₂
Fw	664.63	348.82
Т (К)	293(2) K	100(2) K
λ (Å)	0.71073 Å	0.71073 Å
cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	11.3305(7)	6.8277(2)
b (Å)	11.3887(15)	10.2203(2)
c (Å)	25.9243(16)	18.8056(6)
β (°)	101.672(2)	94.700(2)
V (Å ³)	3276.1(5)	1307.86(6)
Z	4	4
$\rho_{\rm calc} ({\rm Mg/m^3})$	$1.347 {\rm Mg/m^3}$	$1.772 \mathrm{Mg/m^3}$
μ (Mo K α) (mm ⁻¹)	0.576 mm^{-1}	1.690 mm^{-1}
F(000)	1396	708
θ-range	2.180 to 26.341 $^{\circ}$	2.173 to 32.498°
No. reflns.	7685	28,102
Unique reflns.	4249 [R(int) = 0.0414]	4745 [R(int) = 0.0310]
Completeness to theta = 25.242°	64.10%	100.00%
GOOF (F^2)	1.037	1.032
Final R indices $[I > 2sigma(I)]$	$R_1 = 0.0392, wR_2 = 0.0930$	$R_1 = 0.0229, wR_2 = 0.0635$
R indices (all data)	$R_1 = 0.0754, wR_2 = 0.1144$	$R_1 = 0.0264, wR_2 = 0.0657$
CCDC	2,158,205	2,158,206

3. Hirshfeld and DFT Calculations

The topology analyses including Hirshfeld calculations, construction of the different maps (d_{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 [Co(4-Pic)₄(H₂O)(N₃)]NO₃*H₂O*4-Pic; 1

This Co(II) complex crystallizes in the monoclinic crystal system and space group P2₁/c. The unit cell parameters are a = 11.3305(7) Å, b = 11.3887(15) Å, c = 25.9243(16) Å and β = 101.672(2)°, 101.672(2)°, V = 3276.1(5) Å³, Z = 4. Compound **1** is a cationic complex in which the coordination sphere comprises a hexa-coordinated Co(II) ion (Figure 2). There are four Co-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) Å (Co1-N4) to 2.211(3) Å (Co1-N5). The angles of the trans bonds N4-Co1-N6 and N5-Co1-N7 are 178.48(10)° and 175.25(10)°, respectively, while the angles of the *cis* N-Co-N bonds range from 87.04(14)° (N6-Co1-N7) to 93.06(13)° (N4-Co1-N5). 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) Å, respectively, while the O1-Co1-N1 is 178.79(16)° which is very close to the ideal value of 180° (Table 2). Hence the CoN₅O 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.

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

Table 2. Bond lengths (Å) and angles (°) of complex **1**.

The structure of complex **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 ... O2 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.

D-H A	d(D-H)	d(H A)	<dha< th=""><th>d(D A)</th><th>Symmetry Code</th></dha<>	d(D A)	Symmetry Code
O1-H1A O3	0.853	2.568	133.64	3.216	
01-H1A 04	0.853	1.909	170.04	2.753	
O1-H2A O2	0.807	1.859	178.01	2.665	[x + 1, y, z]
O2-H3A N8	0.819	1.973	173.17	2.788	-
O2-H4A O3	0.866	1.953	167.15	2.803	[-x + 1, y - 1/2, -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 O5	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	[x – 1, y, z]
C28-H28 O4	0.93	2.584	168.86	3.501	-
С29-Н29 О5	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 *bc* 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 [Cu(HAld)(Ald)(N₃)]; 2

This Cu(II) complex crystallizes in the monoclinic crystal system and space group $P2_1/n$. The unit cell parameters are a = 6.8277(2) Å, b = 10.2203(2) Å, c = 18.8056(6) Å and $94.700(2)^\circ$, V = 1307.86(6) A³, Z = 4. Compound **2** is a neutral complex in which the Cu(II) is penta-coordinated with the two HAld/Ald⁻ organic ligand combination as bidentate NN-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 [Cu(HAld)(Ald)(N₃)] 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 Cu-N(oxime) in both ligand units. The Cu1-N1 (2.0341(9) Å) and Cu1-N2 (1.9967(9) Å) bonds in one unit are slightly longer than the corresponding Cu1-N3 (2.0480(9) Å) and Cu1-N4 (1.9946(9) Å) bonds in the other ligand unit. The last Cu1-N5 interaction with the azide ligand is the longest (2.2158(10) A). 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

(β = 170.83°) and N2-Cu1-N3 (α = 156.74°) give a $\tau = \frac{(\beta - \alpha)}{60}$ value of 0.24 suggesting as a distorted square pyramid CuN₅ 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 H1 and H2 atoms are not depicted for better clarity.

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

Table 4. Bond lengths (Å) and angles ($^{\circ}$) for complex **2**.

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 O ... H and N ... 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 C-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.

D-H	d(D-H)	d(H A)	<dha a)<="" d(d="" th=""><th>Symmetry Code</th></dha>	Symmetry Code
O1-H1 O2	0.84(3)	1.61(3)	2.4431(13) 174(4)	
С3-Н3 О2	0.95	2.54	3.3761(15) 148	-1/2 + x, $3/2 - y$, $1/2 + z$
C7-H7 N7	0.95	2.57	3.3751(15) 143	1-x, 2-y, -z
С9-Н9 О1	0.95	2.35	3.2252(14) 152	x, 1 + y, z
C10-H10 N5	0.95	2.54	3.2872(15) 136	1/2 - x, $1/2 + y$, $1/2 - z$
C11-H11 N7	0.95	2.51	3.2984(15) 141	1 - x, 2 - y, -z
C12-H12 N6	0.95	2.62	3.4037(15) 140	1/2 - x, $-1/2 + y$, $1/2 - z$

Table 5. Hydrogen bonds in complex 2.

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 . . . N and C-H . . . O interactions along the *ac* plane. The aromatic ring systems are nearly parallel to one another, leading to some π - π stacking interactions which connect the complex units through the *a*-direction (Figure 7B). The shortest C . . . C contacts are C2 . . . C10 (3.383 Å) and C3 . . . C8 (3.325 Å).



Figure 7. Packing scheme of **2** along the monoclinic *b*-axis (**A**) and π - π 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 d_{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 H ... H (53.9%), O ... H (14.1%), N ... H (11.0%) and H ... C (18.8%) interactions (Figure 8). Not all these contacts showed the characteristics of strong interactions. The red spots in the d_{norm} map are related to the short distance O ... H, N ... H and H ... 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 O . . . H interactions which are shorter than the vdWs radii sum of the O and H atoms. Moreover, some significantly short N . . . 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 Å, corresponding to N9 . . . H1A, H3A . . . C25 and O2 . . . H2A contacts, respectively.

In the neutral Cu(II) complex **2**, the crystal stability is controlled by a large number of intermolecular contacts such as the H ... H (27.4%), N ... H (27.7%), O ... H (14.7%), H ... C (13.6%) which are considered the most dominant contacts in the crystal packing (Figure 9). Only the O ... H, N ... H and C ... C interactions appeared as red regions in the d_{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 Å, respectively. Moreover, the SI map showed the characteristic red/blue triangles for the π - π interactions (Figure 9).

2.236



Figure 8. Hirshfeld surfaces and pie chart showing the intermolecular interactions in 1. A–C in the dnorm map belong to the O ... H, N ... H and H ... C contacts, respectively.

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	O4 H28	2.453	O2 H4	2.531

Table 6. Short distance contacts in compounds 1 and 2.

4.3. AIM Studies

The free N_3^- ion is symmetric as the two N-N bonds are equidistant. In contrast, the coordinated azide is asymmetric and the two N-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 Co(II) and Cu(II) complexes. The calculated AIM topological parameters of the N-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 N-N distances are 0.04 and 0.02 Å 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.

O1 . . . H9



Figure 9. Hirshfeld surfaces and pie chart showing the intermolecular interactions in **2**. A–C in the d_{norm} map belong to the O . . . H, N . . . H and C . . . C contacts, respectively.

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

Bond	d _{N-N}	Δd	ρ(r), a.u	$ abla^2 ho(r)^{a}$	V(r)/G(r) ^b
Complex 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

^a Laplacian of electron density; ^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 $\rho(r)$ values of the NA-NB bonds are calculated to be 0.4847 and 0.4833 a.u. in complexes **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 $\rho(r)$ values at the N-N BCPs are higher than 0.1 a.u. and the $\nabla^2 \rho(r)$ 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 M-N and M-O bonds in the studied systems (Table 8). The low electron density ($\rho(r) < 0.10$ au) values and positive H(r) as well as the positive $\nabla^2 \rho(r)$ and V(r)/G(r) < 1 for the Co-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 H(r) and slightly higher V(r)/G(r) than the Co-N(4-Pic). The slightly negative H(r) and V(r)/G(r) marginally higher than 1 for all Cu-N bonds in **2** revealed very few covalent characters. On the other hand, the high $\rho(r)$ values are indicative on the bond strength. As can be seen from Table 8, shorter coordination interaction for a given bond has higher $\rho(r)$ values at the BCP than the longer one.

 $H(r)^{a}; a.u.$ $V(r)/G(r)^{b}$ $\nabla^2 \rho(\mathbf{r})^{c}$ Bond **Bond Length** $\rho(\mathbf{r}); \mathbf{a.u.}$ Complex 1 0.974 Co1-O1 2.091(2)0.0401 0.0023 0.3519 Co1-N1 2.102(3)0.0616 -0.00881.104 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 -0.00501.041 0.4637 Cu1-N2 1.997(1)0.0588 -0.00431.032 0.5258 Cu1-N3 0.0552 -0.00490.4513 2.048(1)1.042 Cu1-N4 1.175 0.0798 -0.01910.3597 1.994(1)Cu1-N5 0.2947 0.0381 0.0000 1.000 2.216(1)

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

^a Total energy density; ^b potential to kinetic energy density; ^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 **1** and **2**, respectively instead of +2. Hence, there is 1.0377 e and 1.2345 e were transferred from the ligand groups to Co(II) and Cu(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 Cu(II) site, respectively.

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

	1		2
Со	0.9623	Cu	0.7655
4-Pic	0.5804	HAld	0.3354
H ₂ O	0.1278	Ald ⁻	-0.7207
N_3^-	-0.7138	N_3^-	-0.7207
NO_3^-	-0.9567		

5. Conclusions

The molecular and supramolecular structures of the monomeric complexes [Co(4-Pic)₄(H₂O)(N₃)]NO₃*H₂O*4-Pic (1) and [Cu(HAld)(Ald)(N₃)] (2) were presented. In complex 1, the CuN₅O coordination geometry is a slightly distorted octahedron while the CuN₅ 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 H … H, O … H, N … H and H … C interactions in 1 based on Hirshfeld

analysis. For **2**, the H ... H, N ... H, O ... H and H ... 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 M-N and M-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**.

Author Contributions: Conceptualization, J.H.A., S.M.S. and M.A.M.A.-Y.; methodology, J.H.A., M.S.A. and A.B.; software, S.M.S., J.H.A.; A.E-F., M.S.A. and A.B.; formal analysis, M.S.A. and J.H.A.; investigation, S.M.S., M.A.M.A.-Y. and J.H.A.; resources, J.H.A., M.S.A. and A.B.; writing—original draft preparation, J.H.A., S.M.S., M.A.M.A.-Y., M.S.A. and A.B.; writing— review and editing, J.H.A., S.M.S., M.A.M.A.-Y., M.S.A. and A.B.; supervision, S.M.S. and M.A.M.A.-Y.; project administration, J.H.A., A.B., S.M.S. and M.A.M.A.-Y. and funding acquisition, M.S.A., A.B. All authors have read and agreed to the published version of the manuscript.

Funding: Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R86), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Data Availability Statement: Not applicable.

Acknowledgments: Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R86), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Mir, M.H.; Koh, L.L.; Tan, G.K.; Vittal, J.J. Single-Crystal to Single-Crystal Photochemical Structural Transformations of Interpenetrated 3 D Coordination Polymers by [2 + 2] Cycloaddition Reactions. *Angew. Chem. Int. Ed.* 2010, 49, 390–393. [CrossRef] [PubMed]
- Das, L.K.; Gómez-García, C.J.; Ghosh, A. Influence of the central metal ion in controlling the self-assembly and magnetic properties of 2D coordination polymers derived from [(NiL)₂M]₂ + nodes (M = Ni, Zn and Cd) (H₂L = salen-type di-Schiff base) and dicyanamide spacers. *Dalton Trans.* 2015, 44, 1292–1302. [CrossRef] [PubMed]
- Das, L.K.; Diaz, C.; Ghosh, A. Antiferromagnetic mixed-valence Cu(I)–Cu(II) two-dimensional coordination polymers constructed by double oximato bridged Cu(II) dimers and CuISCN based one-dimensional anionic chains. *Cryst. Growth Des.* 2015, 15, 3939–3949. [CrossRef]
- 4. Yamada, T.; Otsubo, K.; Makiura, R.; Kitagawa, H. Designer coordination polymers: Dimensional crossover architectures and proton conduction. *Chem. Soc. Rev.* 2013, 42, 6655–6669. [CrossRef]
- Li, H.; Wang, Y.; He, Y.; Xu, Z.; Zhao, X.; Han, Y. Synthesis of several novel coordination complexes: Ion exchange, magnetic and photocatalytic studies. *New J. Chem.* 2017, 41, 1046–1056. [CrossRef]
- Mondal, M.; Jana, S.; Drew, M.G.; Ghosh, A. Application of two Cu(II)-azido based 1D coordination polymers in optoelectronic device: Structural characterization and experimental studies. *Polymer* 2020, 204, 122815. [CrossRef]
- Zhang, Z.; Zhao, Y.; Gong, Q.; Li, Z.; Li, J. MOFs for CO₂ capture and separation from flue gas mixtures: The effect of multifunctional sites on their adsorption capacity and selectivity. *Chem. Commun.* 2013, 49, 653–661. [CrossRef]
- Zeng, L.W.; Hu, K.Q.; Mei, L.; Li, F.Z.; Huang, Z.W.; An, S.W.; Chai, Z.F.; Shi, W.Q. Structural diversity of bipyridinium-based uranyl coordination polymers: Synthesis, characterization, and ion-exchange application. *Inorg. Chem.* 2019, 58, 14075–14084. [CrossRef]
- 9. He, Y.; Li, B.; O'Keeffe, M.; Chen, B. Multifunctional metal–organic frameworks constructed from meta-benzenedicarboxylate units. *Chem. Soc. Rev.* 2014, 43, 5618–5656. [CrossRef]
- Lee, M.M.; Kim, H.Y.; Hwang, I.H.; Bae, J.M.; Kim, C.; Yo, C.H.; Kim, Y.; Kim, S.J. Cd II MOFs Constructed Using Succinate and Bipyridyl Ligands: Photoluminescence and Heterogeneous Catalytic Activity. *Bull. Korean Chem. Soc.* 2014, 35, 1777–1783. [CrossRef]
- 11. Dutta, B.; Jana, R.; Bhanja, A.K.; Ray, P.P.; Sinha, C.; Mir, M.H. Supramolecular aggregate of Cadmium (II)-based one-dimensional coordination polymer for device fabrication and sensor application. *Inorg. Chem.* **2019**, *58*, 2686–2694. [CrossRef] [PubMed]
- Ghorai, P.; Dey, A.; Brandão, P.; Benmansour, S.; Gómez García, C.J.; Ray, P.P.; Saha, A. Multifunctional Ni(II)-Based Metamagnetic Coordination Polymers for Electronic Device Fabrication. *Inorg. Chem.* 2020, 59, 8749–8761. [CrossRef] [PubMed]

- 13. Liu, J.Q.; Luo, Z.D.; Pan, Y.; Singh, A.K.; Trivedi, M.; Kumar, A. Recent developments in luminescent coordination polymers: Designing strategies, sensing application and theoretical evidences. *Coord. Chem. Rev.* **2020**, 406, 213145. [CrossRef]
- 14. Zhang, X.; Wang, W.; Hu, Z.; Wang, G.; Uvdal, K. Coordination polymers for energy transfer: Preparations, properties, sensing applications, and perspectives. *Coord. Chem. Rev.* **2015**, *284*, 206–235. [CrossRef]
- Xie, Z.; Ma, L.; de Krafft, K.E.; Jin, A.; Lin, W. Porous phosphorescent coordination polymers for oxygen sensing. J. Am. Chem. Soc. 2010, 132, 922–923. [CrossRef]
- 16. Alsharabasy, A.M.; Pandit, A.; Farràs, P. Recent Advances in the Design and Sensing Applications of Hemin/Coordination Polymer-Based Nanocomposites. *Adv. Mater.* 2021, *33*, 2003883. [CrossRef] [PubMed]
- Stavila, V.; Talin, A.A.; Allendorf, M.D. MOF-based electronic and opto-electronic devices. *Chem. Soc. Rev.* 2014, 43, 5994–6010. [CrossRef]
- Dhakshinamoorthy, A.; Garcia, H. Catalysis by metal nanoparticles embedded on metal–organic frameworks. *Chem. Soc. Rev.* 2012, 41, 5262–5284. [CrossRef]
- Allendorf, M.D.; Bauer, C.A.; Bhakta, R.K.; Houk, R.J.T. Luminescent metal–organic frameworks. *Chem. Soc. Rev.* 2009, 38, 1330–1352. [CrossRef]
- Roy, S.; Halder, S.; Drew, M.G.; Ray, P.P.; Chattopadhyay, S. Fabrication of an active electronic device using a hetero-bimetallic coordination polymer. ACS Omega 2018, 3, 12788–12796. [CrossRef]
- 21. Kar, P.; Guha, P.M.; Drew, M.G.; Ishida, T.; Ghosh, A. Spin-Canted Antiferromagnetic Phase Transitions in Alternating Phenoxoand Carboxylato-Bridged MnIII-Salen Complexes. *Eur. J. Chem.* **2011**, 2011, 2075–2085. [CrossRef]
- 22. Lide, D.R. Handbook of Chemistry and Physics, 87th ed.; CRC Press: Boca Raton, FL, USA, 1998; pp. 4–55.
- 23. Patnaik, P. Handbook of Inorganic Chemicals; The McGraw-Hill Companies Inc.: New York, NY, USA, 2003; pp. 460–461.
- 24. Betterton, E.A. Environmental Fate of Sodium Azide Derived from Automobile Airbags. *Crit. Rev. Environ. Sci. Technol.* 2003, 33, 423–458. [CrossRef]
- Wang, L.-Y.; Zhao, B.; Zhang, C.-X.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P. The First Azide (μ1,1)-Bridged Binuclear Cobalt(II)–Imino Nitroxide Complex with Ferromagnetic Behavior. *Inorg. Chem.* 2003, 42, 5804–5806. [CrossRef] [PubMed]
- Wang, X.-Y.; Wang, L.; Wang, Z.-M.; Gao, S. Solvent-Tuned Azido-Bridged Co²⁺ Layers: Square, Honeycomb, and Kagome. J. Am. Chem. Soc. 2006, 128, 674–675. [CrossRef] [PubMed]
- Wang, X.-T.; Wang, Z.-M.; Gao, S. Honeycomb Layer of Cobalt(II) Azide Hydrazine Showing Weak Ferromagnetism. *Inorg. Chem.* 2007, 46, 10452–10454. [CrossRef] [PubMed]
- Palenik, G.H. The Structure of Coordination Compounds. I. The Crystal and Molecular Structure of AzidoPentamminecobalt(III) Azide. Acta Crystallogr. 1964, 17, 360–367. [CrossRef]
- 29. Housecroft, C.E.; Constable, E.C. The Emergence of Copper(I)-based Dye Sensitized Solar Cells. *Chem. Soc. Rev.* 2015, 44, 8386–8398. [CrossRef] [PubMed]
- 30. Safin, D.A.; Frost, J.; Murugesu, M. The Renaissance of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) Coordination Chemistry. *Dalton Trans.* 2015, 44, 20287–20294. [CrossRef]
- 31. Case, F.H.; Koft, E.J. The Synthesis of Certain Substituted 1,3,5-Triazines Containing the Ferroin Group. *Am. Chem. Soc.* **1959**, *81*, 905–906. [CrossRef]
- 32. Liu, X.H.; Krott, M.; Müller, P.; Hu, C.H.; Lueken, H.; Dronskowski, R. Synthesis, Crystal Structure, and Properties of MnNCN, the First Carbodiimide of a Magnetic Transition Metal. *Inorg. Chem.* **2005**, *44*, 3001–3003. [CrossRef]
- Liao, W.P.; Hu, C.H.; Kremer, R.K.; Dronskowski, R. Formation of Complex Three- and One-dimensional Interpenetrating Networks Within Carbodiimide Chemistry: NCN^{2–}-Coordinated Rare-Earth-Metal Tetrahedra and Condensed Alkali-metal Iodide Octahedra in Two Novel Lithium Europium Carbodiimide Iodides, LiEu₂(NCN)I₃ and LiEu₄(NCN)₃I₃. *Inorg. Chem.* 2004, 43, 5884–5890. [PubMed]
- Liao, W.P.; Dronskowski, R. Crystal Structures of Extended Europium Cyanamide–Carbodiimide Compounds Derived from Different Reaction Conditions: Temperature-Controlled Syntheses of In_{0.08}Eu₄(NCN)₃I₃, Eu₈I₉(CN)(NCN)₃, and In_{0.28}Eu₁₂(NCN)5I_{14.91}. *Inorg. Chem.* 2006, 45, 3828–3830. [CrossRef] [PubMed]
- Srinivasan, R.; Ströbele, M.; Meyer, H. Chains of [RE₆] Octahedra Coupled by (NCN) Links in the Network Structure of RE₂Cl(CN₂)N. Synthesis and Structure of Two Novel Rare Earth Chloride Carbodiimide Nitrides with Structures Related to the RE₂Cl₃ Type. J. Inorg. Chem. 2003, 42, 3406–3411. [CrossRef] [PubMed]
- 36. Gütlich, P.; Carcia, Y.; Goodwin, H.A. Spin Crossover Phenomena in Fe(II) Complexes: Dedicated to Professor F. A. Cotton on Occasion of his 70th Birthday. *Chem. Soc. Rev.* 2000, *29*, 419–427. [CrossRef]
- 37. Gütlich, P.; Goodwin, H.A. Spin Crossover in Transition Metal Compounds I; Springer: Berlin/Heidelberg, Germany; New York, NY, USA, 2004; pp. 1–342.
- Gaspar, A.B.; Ksenofontov, V.; Seredyuk, M.; Gütlich, P. Multifunctionality in Spin Crossover Materials. Coord. Chem. Rev. 2005, 249, 2661–2676.
- 39. Yu, F.; Xiang, M.; Li, A.H.; Zhang, Y.M.; Li, B. Structural Diversities and Magnetic Properties of Azide-containing Coordination Polymers Based on Flexible Tetra-Pyridinate Ligands. *CrystEngComm* **2015**, *17*, 1556–1563. [CrossRef]
- 40. Ershova, I.V.; Bogomyakov, A.S.; Rumyantsev, R.V.; Fukin, G.K.; Piskunov, A.V. Pentacoordinated Manganese(III) Bis-oiminobenzosemiquinonates: Looking for Spin-crossover Phenomenon. J. Mol. Struct. 2021, 1225, 129092. [CrossRef]

- 41. Ershova, I.V.; Bogomyakov, A.S.; Kubrin, S.P.; Cherkasov, A.V.; Piskunov, A.V. Iron(III) Complexes Based on N-Benzylidene-2-Hydroxy-3,5-Di-tert-Butylaniline. *Russ. J. Coord. Chem.* **2021**, *47*, 1–9. [CrossRef]
- 42. Vasilchenko, D.B.; Zadesenets, A.V.; Baidina, I.A.; Piryazev, D.A.; Romanenko, G.V. Crystal Structures of Dis-diiododiammine Platinum and Trans-diazidodiammine Platinum. *J. Struct. Chem.* **2017**, *58*, 1689–1692. [CrossRef]
- 43. Sheldrick, G.M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; ScienceOpen: Burlington, VT, USA, 1996.
- 44. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Crystallogr. C Struct. Chem. 2015, 71, 3–8. [CrossRef]
- 45. Spackman, M.A.; Jayatilaka, D. Hirshfeld Surface Analysis. CrystEngComm 2009, 11, 19–32. [CrossRef]
- Hirshfeld, F.L. Bonded-Atom Fragments for Describing Molecular Charge Densities. Theor. Chim. Acta 1977, 44, 129–138. [CrossRef]
- Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Spackman, P.R.; Jayatilaka, D.; Spackman, M.A. Crystal Explorer17; University of Western Australia: Crawley, Australia, 2017. Available online: https://crystalexplorer.net/download/ (accessed on 30 July 2019).
- Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *GAUSSIAN 09*; Revision A02; Gaussian Inc.: Wallingford, CT, USA, 2009.
- 49. Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. NBO; Version 3.1, CI; University of Wisconsin: Madison, WI, USA, 1998.
- 50. Chai, J.D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620. [CrossRef] [PubMed]
- 51. Bader, R.F.W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, UK, 1990.
- 52. Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comp. Chem. 2012, 33, 580–592. [CrossRef] [PubMed]
- Addison, A.W.; Rao, T.N.; Reedijk, J.; Rijn, J.V.; Verschoor, G.C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen–Sulphur Donor Ligands; The Crystal and Molecular Structure of Aqua [1,7-bis(Nmethylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate. J. Chem. Soc. Dalton Trans. 1984, 7, 1349–1356. [CrossRef]
- 54. Evans, L.B.; Yofee, A.D.; Gray, P. Physics and Chemistry of the Inorganic Azides. Chem. Rev. 1959, 59, 515–568. [CrossRef]
- 55. Pauling, L. The Natural of the Chemical Bond; Cornell University Press: Ithaca, NY, USA, 1967.
- 56. Matta, C.F.; Hernandez-Trujillo, J.; Tang, T.-H.; Bader, R.F.W. Hydrogen–Hydrogen Bonding: A Stabilizing Interaction in Molecules and Crystals. *Chem. Eur. J.* 2003, *9*, 1940–1951. [CrossRef]
- Grabowski, S.J.; Pfitzner, A.; Zabel, M.; Dubis, A.T.; Palusiak, M.; Intramolecular, H.H. Interactions for the Crystal Structures of [4-((E)-But-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate and [4-((E)-Pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3carboxylate; DFT Calculations on Modeled Styrene Derivatives. J. Phys. Chem. B 2004, 108, 1831–1837. [CrossRef]
- 58. Matta, C.F.; Castillo, N.; Boyd, R.J. Characterization of a Closed-Shell Fluorine–Fluorine Bonding Interaction in Aromatic Compounds on the Basis of the Electron Density. *J. Phys. Chem. A* 2005, *109*, 3669–3681. [CrossRef]
- 59. Pendás, A.M.; Francisco, E.; Blanco, M.A.; Gatti, C. Bond Paths as Privileged Exchange Channels. *Chem. Eur. J.* 2007, 13, 9362–9371. [CrossRef]
- 60. Gibbs, G.V.; Cox, D.F.; Crawford, T.D.; Rosso, K.M.; Ross, N.L.; Downs, R.T. Classification of Metal-oxide Bonded Interactions Based on Local potential and Kinetic-energy Densities. J. Chem. Phys. 2006, 124, 084704. [CrossRef] [PubMed]
- 61. Dinda, S.; Samuelson, A.G. The Nature of Bond Critical Points in Dinuclear Copper(I) Complexes. *Chem. Eur. J.* **2012**, *18*, 3032–3042. [CrossRef] [PubMed]
- 62. Cremer, D.; Kraka, E. Chemical Bonds without Bonding Electron Density—Does the Difference Electron-Density Analysis Suffice for a Description of the Chemical Bond? *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627–628. [CrossRef]
- 63. Jenkins, V.; Morrison, I. The Chemical Character of The Intermolecular Bonds of Seven Phases of Ice as Revealed by AB initio Calculation of Electron Densities. *Chem. Phys. Lett.* **2000**, *317*, 97–102. [CrossRef]
- 64. Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. From Weak to Strong interactions: A Comprehensive Analysis of the Topological and Energetic Properties of the Electron Density Distribution Involving X–H . . . F–Y Systems. *J. Chem. Phys.* 2002, *117*, 5529–5542. [CrossRef]
- Varadwaj, P.R.; Marques, H.M. The Physical Chemistry of Coordinated Aqua-, Ammine-, and Mixed-ligand Co²⁺ Complexes: DFT Studies on the Structure, Energetics, and Topological Properties of the Electron Eensity. *Phys. Chem. Chem. Phys.* 2010, 12, 2126–2138. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.