

# Highly Efficient Synthesis of Complex bis-2,4-dimethoxy-1,3,5-triazapentadienemetal(II) (metal = Cu, Ni) with Hirshfeld Surface Analysis

I Wayan Dasna<sup>a,b,\*</sup>, Husni Wahyu Wijaya<sup>a,b</sup>, Faaza'izzahq Setta Putra<sup>a</sup>, Hakam Abdulloh<sup>a</sup>, Ahmad Taufiq<sup>a,c</sup>

<sup>a</sup>Department of Chemistry, State University of Malang (Universitas Negeri Malang), Jl. Semarang 5, Malang, Jawa Timur, Indonesia 65145; <sup>b</sup>Centre of Advanced Material for Renewable Energy, State University of Malang (Universitas Negeri Malang), Jl. Semarang 5 Malang, Jawa Timur, Indonesia 65145; <sup>c</sup>Department of Physics, State University of Malang (Universitas Negeri Malang), Jl. Semarang 5, Malang, Jawa Timur, Indonesia 65145

**Abstract** The synthesis of copper(II) or Nickel(II) complex with bis-2,4-dimethoxy-1,3,5-triazapentadiene ligand has been reported using a direct reaction and reflux method. These methods take a relatively long synthesis time, so it is necessary to develop a faster synthesis method. This study reports a solvothermal method to synthesize bis-2,4-dimethoxy-1,3,5-triazapentadiene copper(II) and nickel(II) as in situ with sodium dicyanamide and methanol that produces single crystals in a day and two days respectively. XRD analysis of both single crystals from solvothermal results showed a monoclinic crystal lattice and a P21/n space group which was not different from previous studies. The Hirshfeld analysis indicates that the interactions with the most prevelant contributions in both of complexes are H—H, O—H/H—O, and N—H/N—H.

**Keywords:** Copper(II) complex, nickel(II) complex, 2,4-methoxy-1,3,5-triazapentadiene ligand, solvothermal, Hirshfeld surface analysis.

## Introduction

Compounds with imine groups ( $C=N$ ) have been widely used, especially as catalysts in organic reactions that involve carboxylation and cross-coupling of C—C [1], [2]. This compound could also be used as an inhibitory enzyme, biomimetic material, and analytical chemistry [1], [3]. Complex compounds with an imine ligand, such as 2,4-dimethoxy-1,3,5-triazapentadiene (TAP) and their derivatives, have a high degree of stability and solubility in halocarbon solvents, so they are often used as chelating agents in coordination compounds [4]–[6].

The first known complex compound with the TAP ligand is bis-2,4-dimethoxy-1,3,5-triazapentadiene copper(II) or  $Cu(TAP)_2$ . The compound is difficult to synthesize because it requires a long process with a low-reaction product. The compound  $Cu(TAP)_2$  complex can also be used as a precursor material to synthesize other TAP complex compounds, such as bis-2,4-dimethoxy-1,3,5-triazapentadiene nickel(II) or  $Ni(TAP)_2$  through the reaction between  $Cu(TAP)_2$  with nickel hydroxide and acetylacetic acid while stirring at room temperature, 25°C for 6 hours. The orange precipitate formed was then recrystallized with acetone as a solvent [7]. In this reaction, a substitution reaction of the central ion  $Cu^{2+}$  by  $Ni^{2+}$  occurs, which can occur because the reactivity of the nickel(II) ion is greater than that of the copper(II) ion.

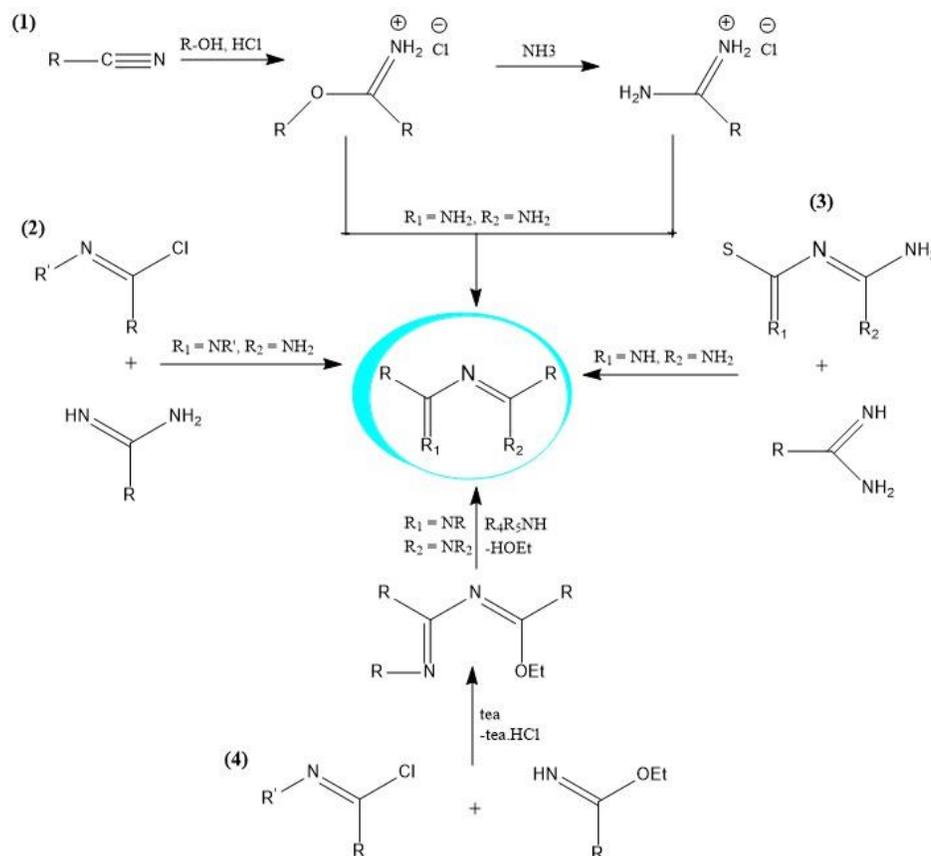
\*For correspondence:  
idasna@um.ac.id

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Figure 1 describes the synthesis of TAP compounds was carried out by several methods, such as the Pinner synthesis by reacting the imino ester (RC(=NH)OR) with amidine (RC(=NH)NH<sub>2</sub>), the NH<sub>2</sub> group on the amidine bound to the C atom of the C = N group of the imino ester to form the TAP compound, but the yield produced is relatively small. The Ley and Muller Muller *et al.* [8] synthesis method was carried out by reacting N-imidoyl chloride with amidine, although the TAP compound produced from this method was difficult to isolate [1]. The amination of N-imidoylimidoate is the development of Ley and Muller *et al.* [8]. In the synthesis method, N-imidoyl chloride is reacted with imidoate by adding triethanolamine (tea) to produce N-imidoimididoate. The resulting compound is reacted with an amine to produce TAP. Desulfuration amination or amidination of N-thiobenzoylbenzamide is carried out by reacting N-thioamidine with thiobenzamide and phenyl cyanide under hydrochloric acid gas conditions. The obtained N-thiobenzoylbenzamide is desulfurized with amine or amidine to produce TAP.



**Figure 1.** TAP synthesis method, Pinner method (1), Ley and Muller method (2), desulfuration amination or amidination of N-thiobenzoylbenzamide (3), and amination of N-imidoylimidoate (4)

The Ley and Muller *et al.* [8] synthesis method has been widely developed to synthesize many TAP derivative compounds [9]. However, the previous methods have low time efficiency to the long synthesis process. Its compound must be required in large quantities for catalyst application with a simpler and faster synthesis method. The complex compound Cu (TAP)<sub>2</sub> have been synthesized using different methods from Boċa *et al.* [10] and Kopylovich *et al.* [11] but still needs a long process.

The synthesis of the compound Ni(TAP)<sub>2</sub> used a different process than that of Cu(TAP)<sub>2</sub>. The synthesis of Ni(TAP)<sub>2</sub> reported by Andrusenko *et al.* [12] used the direct reaction method. The NiCl<sub>2</sub> salt was dissolved in 3 mL of methanol and then added with NCN(CH<sub>3</sub>)<sub>2</sub>. The mixture is then stirred at room temperature for 2 weeks (or at 50°C for 3 days) in a closed container. The color of the solution changes to a bright green color during the reaction process, and the mixture is then filtered. The filtrate from the filtrate was evaporated at room temperature for 2 days to produce orange crystals. The reaction process above takes a relatively long time to obtain crystals with a yield of 35% (39%, 50 °C 3 days) [3].

The solvent method used by Zhao *et al.* [13] in 2006 to produce  $\text{Cu}(\text{TAP})_2$  compounds, first copper (II), first copper acetate (II), sodium dicyanamide, and 3-hydroxy-3-methoxycarbonyl pentadionic acid are mixed and dissolved in 10 mL of methanol. The mixture was then placed in the autoclave to be further heated at 140 °C for 3 days. After the heating reaction, the autoclave was slowly cooled (5  $\text{K h}^{-1}$ ). The purplish red needle-shaped crystals were obtained by filtration, and the crystals were di- $\mu$ -methoxy-bis[[bis(methoxycarbimido)-aminato] copper(II)] compounds. The filtrate obtained evaporates for several days and produces red crystals as blocks [13]. The crystal structure of  $\text{Cu}(\text{TAP})_2$  and  $\text{Ni}(\text{TAP})_2$  from Boca *et al.* [10] and Andrusenko *et al.* [3] given a square planar manner but have a little difference in terms of bond length and angle with  $\text{Cu}(\text{TAP})_2$  and  $\text{Ni}(\text{TAP})_2$  from this work.

Based on the study of complex synthesis methods with TAP ligands, it is known that TAP ligands can be formed in the reflux process between sodium dicyanamide and methanol, and the reaction can occur under hot conditions. Based on the reaction process in the previous synthesis, reflux and solvothermal techniques can provide a shorter reaction time because heating is carried out at high pressure in an autoclave. The formation of TAP from Na-dca and methanol can occur in the reflux process so that in situ synthesis of the  $\text{M}(\text{TAP})_2$  complex ( $\text{M} = \text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) can occur. This study modified the solvothermal synthesis method of Zhao *et al.* [13] in 2006, where the TAP ligand was synthesized in situ by direct reaction in an autoclave under high temperature and pressure conditions. In this reaction, the nucleophilic attack of methanol can occur against the cyano group, that dicyanamide can be dissolved, causing TAP ligands to form faster.

In this study, we reported a highly efficient as-synthesized  $\text{Cu}(\text{TAP})_2$  and  $\text{Ni}(\text{TAP})_2$  formed using TAP ligand generated in situ from the reaction between Na-dca and methanol using the solvothermal method. TAP ligand formed in situ then reacted with nickel(II) or copper(II) ion giving crystal of  $\text{M}(\text{TAP})_2$  ( $\text{M} = \text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ). The single crystals were obtained directly after autoclaving the solvothermal reaction. The structure of the as-synthesized complexes is a critical study in this report.

## Materials and Methods

All materials were purchased from Merck and Sigma Aldrich at high purity. All salts such as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (p.a, Merck),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (p.a, Merck),  $\text{ZnCl}_2$  (p.a, Sigma Aldrich),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (p.a, Merck), ligand  $\text{NaN}(\text{CN})_2$  (p.a, Sigma Aldrich), and methanol (p.a, Merck) were directly used without additional treatment.

### Instrumentation

Melting point measurements of the crystals were carried out with the Fisher-John Melting Point Apparatus, and the determination of the levels of Cu and Ni in the complex was carried out using the AAS (Thermo Fischer), while electrical conductivity was measured with a conductometer. Determination of the structure of the complex compound used a single crystal XRD (Bruker D8 Quest Eco), and infrared spectra was measured with a Shimadzu FT-IR instrument.

### Synthesis procedure

The as-synthesized of  $\text{Cu}(\text{TAP})_2$  or  $[\text{Cu}\{\text{N}[\text{C}(\text{NH})\text{OCH}_3]_2\}_2]$  was obtained by mixing copper(II) chloride (0.08524 gram; 0.5 mmol) and sodium dicyanamide (0.08903 gram; 1 mmol), each of which was dissolved with 5 ml of methanol with stirring for 10 minutes to obtain a green solution, was transferred into teflon autoclave and then heated at 70 °C for 5 h. After 5 h, the solution in the autoclave was cooled at room temperature overnight to obtain purplish-red needle-shaped crystals. Needle red purplish crystals gave 91% yield, melted at 242–245 °C, and contained 21 % of Cu from AAS (theory = 19%). The unique vibration from FTIR showed as follow  $\tilde{\nu} = 3344$  (s)  $\nu(\text{O} - \text{H})$ ; 2951 (m-w)  $\nu(\text{C} - \text{H})$ ; 1604 (s)  $\nu(\text{N} = \text{H})$ ; 1531 (s)  $\delta(\text{N} - \text{H})$ .

The as-synthesized  $\text{Cu}(\text{TAP})_2$  was obtained with similar protocols by changing nickel salt with copper salt synthesis method was carried out by dissolving copper(II) chloride (0.08524 gram; 0.5 mmol), cobalt(II) chloride solution (0.118965 gram; 0.5 mmol), and sodium dicyanamide (0.17806 grams; 2 mmol) each with 5 mL of methanol and mixed for 10 minutes, a brown solution was obtained. Solvothermal treatment was carried out at 100°C for 5 hours. Needle-shaped purplish-red crystals were obtained after the solvothermal reaction, and the crystals were filtered and separated from the filtrate. The filtrate was evaporated at room temperature within 3-4 days to obtain dark red crystals. Dark red crystal in the form of a block, yield = 86%, TL = 243–245°C, Cu(AAS): 18% (theory=19%), FTIR:  $\tilde{\nu} = 3342$  (s)  $\nu(\text{O} - \text{H})$ ; 2953 (m-w)  $\nu(\text{C} - \text{H})$ ; 1606 (s)  $\nu(\text{N} = \text{H})$ ; 1566 (s)  $\delta(\text{N} - \text{H})$ .

The as-synthesized of Ni(TAP)<sub>2</sub> or [Ni{N[C(NH)OCH<sub>3</sub>]<sub>2</sub>}]<sub>2</sub> was obtained by reacting 2 mmol of sodium dicyanamide (0.178 grams) dissolved in 5 mL of methanol and 0.5 mmol of zinc(II) chloride (0.068 grams) dissolved in 5 ml of methanol to produce a colorless solution and then transferred into the autoclave and heated at 70 °C for 16 h to produce a colorless solution and a white precipitate. After cooling at room temperature, 0.5 mmol of nickel(II) chloride (0.118 grams) in 5 mL methanolic solution was added, giving orange solution, then heated (in autoclave) at 100 °C for 5 h. After cooling, the solution was filtered, and orange needle-shaped crystals were obtained, yield = 47%, Melting Point = 243–245°C, Ni(AAS): 24.9% (theory = 18%), FTIR:  $\tilde{\nu}$  = 3331 (s)  $\nu$ (O – H); 2992 (m-w)  $\nu$ (C – H).

### X-ray Crystallography

Single crystal of the as-synthesized complexes was selected, and their intensity data were measured with the crystal at 296 K using D8 QUEST Eco PHOTON II equipped with an APEX4 with Mo Ka radiation. Non-hydrogen-atom positions were determined by Fourier difference map analyses with refinements carried out with the SHELXL package using full-matrix least squares on F<sup>2</sup> with anisotropic displacement parameters. The positions of all H-atoms in the structure were established and refined using a riding model.

## Results and Discussion

### Solvothermal Method Synthesis of M(TAP)<sub>2</sub> (M = Cu, Ni)

The solvothermal method is a development of the hydrothermal method, which is differentiated by the solvent. The solution inside the autoclave was heated above the solvent's boiling point to become a gas. The gases then exerted pressure on the autoclave during the reaction, accelerating the chemical reaction process. TAP compounds can be formed in situ where the cyano group on dicyanamide reacted with methanol giving imine group [1].

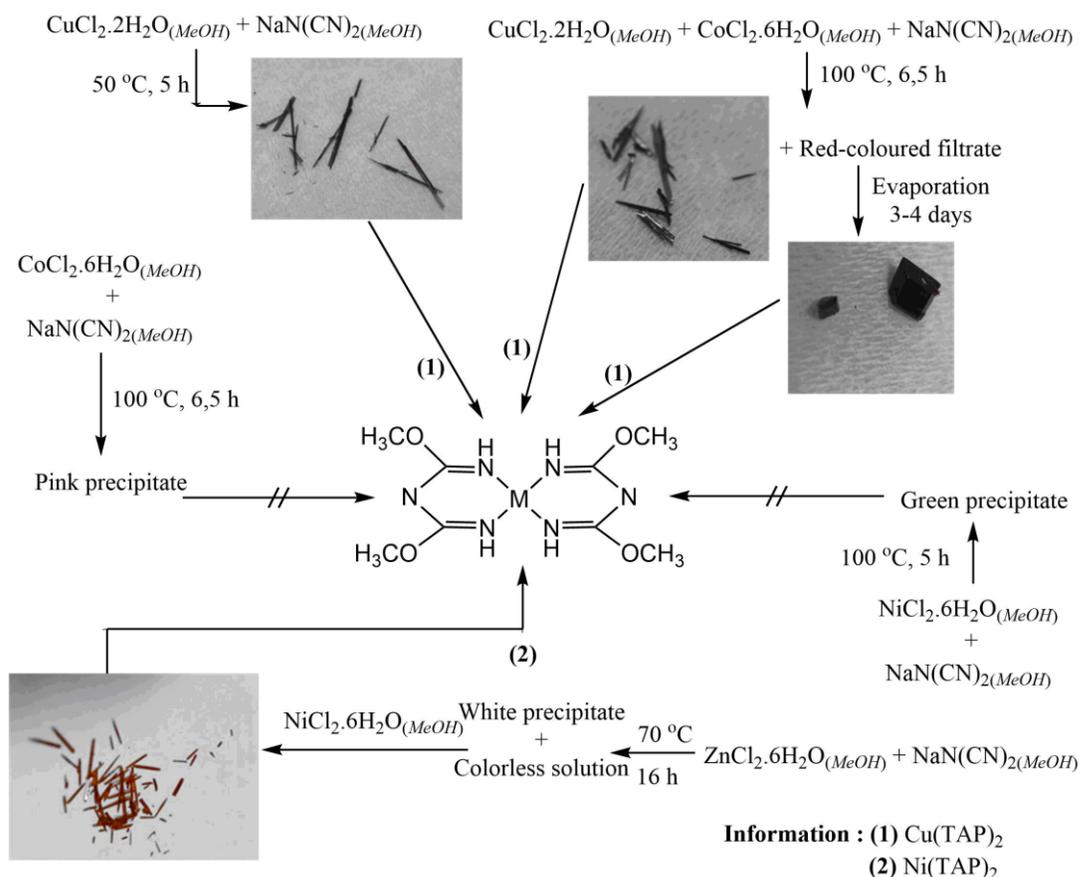
This research is more efficient than the method used by Zhao *et al.* [14] because our reaction only used solvothermal at a lower temperature than 140 °C and less than 24 h. Modifications were made to synthesize Cu(TAP)<sub>2</sub> compounds using the faster solvothermal method and to synthesize Ni(TAP)<sub>2</sub> compounds using the solvothermal method, which had never been done before. In this process, TAP ligands can be formed in situ following the reaction mechanism described by Kopylovich *et al.* [1].

Table 1 shows the differences between the Cu(TAP)<sub>2</sub> and Ni(TAP)<sub>2</sub> synthesis methods in this study and published studies. The data in the table show that using the solvothermal method in this study is more effective in reducing the reaction and crystallization time. The solvothermal method used in this study showed that the manufacture of TAP ligands from dicyanamide anions took place more quickly due to the influence of heating and pressure in the autoclave in an isolated system. The use of temperatures above the solvent's boiling point causes the solvent to evaporate and increases the pressure in the system, increasing the reaction rate. When the reaction is stopped and the cooling process occurs, a decrease in the system's temperature causes the crystallization process to occur directly. The solvothermal reaction flow for the formation of the as-synthesized M(TAP)<sub>2</sub> crystals in this study is presented in Figure 2.

Figure 2 shows that the compound Cu(TAP)<sub>2</sub> can be synthesized using the solvothermal method by reacting CuCl<sub>2</sub>·2H<sub>2</sub>O with NaN(CN)<sub>2</sub> in a methanol solvent. This reaction is the shortest process to make Cu(TAP)<sub>2</sub>. The second method, synthesis using a mixed salt, namely CuCl<sub>2</sub>·2H<sub>2</sub>O and CoCl<sub>2</sub>·6H<sub>2</sub>O, dissolved in methanol and an added NaN(CN)<sub>2</sub> solution (in methanol) can also produce Cu(TAP)<sub>2</sub> crystals which are the same as the crystals that precipitate directly in the autoclave or the evaporation of the filtrate. Despite their different shapes, both crystals have the same color and melting point. However, the synthesis of the Co(TAP)<sub>2</sub> compound by reacting CoCl<sub>2</sub>·2H<sub>2</sub>O and NaN(CN)<sub>2</sub> salts in methanol solvent using the same solvothermal method to synthesize and synthesize Cu(TAP)<sub>2</sub> was not successful. The same case occurred in synthesizing compound Ni(TAP)<sub>2</sub> through the reaction between NiCl<sub>2</sub>·6H<sub>2</sub>O salt and NaN(CN)<sub>2</sub> in methanol solvent; the solvothermal result obtained was a green precipitate. The method was modified to synthesize Ni(TAP)<sub>2</sub> by solvothermal reacting the ZnCl<sub>2</sub>·6H<sub>2</sub>O salt with NaN(CN)<sub>2</sub> in methanol solvent, resulting in a colorless solution and a white precipitate. The NiCl<sub>2</sub>·6H<sub>2</sub>O solution was then mixed into the mixture and heated in a solvothermal autoclave. The results of the stepwise reaction produced crystals of Ni(TAP)<sub>2</sub> directly. Based on this pathway, Ni(TAP)<sub>2</sub> cannot be obtained directly from the solvothermal reaction between Ni<sup>2+</sup> salt and NaN(CN)<sub>2</sub> in methanol as-synthesized Cu(TAP)<sub>2</sub>. The Ni(TAP)<sub>2</sub> complex was obtained through the substitution reaction of Zn<sup>2+</sup> by Ni<sup>2+</sup> in solution.

**Table 1.** Analysis of differences in synthetic methods with previous research

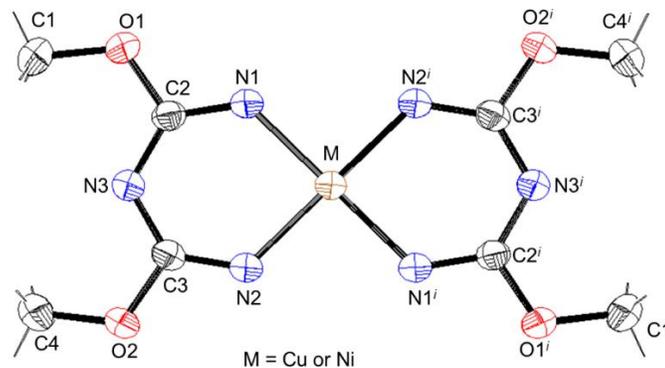
	Cu(TAP) <sub>2</sub> [14]	The as-synthesized Cu(TAP) <sub>2</sub>	Ni(TAP) <sub>2</sub> [3]	The as-synthesized Ni(TAP) <sub>2</sub>
Method	Solvothermal	Solvothermal	Direct Reaction	Solvothermal
Material	Cu(OAc) <sub>2</sub> , NaN(CN) <sub>2</sub> , C <sub>7</sub> H <sub>10</sub> O <sub>7</sub>	CuCl <sub>2</sub> , NaN(CN) <sub>2</sub>	NCN(CH <sub>3</sub> ) <sub>2</sub> , NiCl <sub>2</sub>	NiCl <sub>2</sub> , NaN(CN) <sub>2</sub>
Solvent	CH <sub>3</sub> OH	CH <sub>3</sub> OH	CH <sub>3</sub> OH	CH <sub>3</sub> OH
Reaction temperature (°C)	140 °C	70 °C	a. Room temperature 50 °C	70 °C + 100 °C
Reaction time	3 days	5 hours	a. 14 days 3 days	16 hours + 5 hours
Crystallization time	A couple of days	A night	2 days	A night
Yield	40%	91%	40%	47%



**Figure 2.** Synthesis strategy of The as-synthesized of M(TAP)<sub>2</sub> (M = Cu, Ni) using solvothermal method.

### Single Crystal X-ray Diffraction Analysis

Our synthesis strategy produced needle-shaped purplish red crystals for The as-synthesized Cu(TAP)<sub>2</sub> and needle-shaped orange crystals for The as-synthesized Ni(TAP)<sub>2</sub>. The structure and crystallographic data of the compounds synthesized with Cu(TAP)<sub>2</sub> with Cu (TAP)<sub>2</sub> and Ni (TAP)<sub>2</sub> in this study are presented in Figure 3 and Table 2.



**Figure 3.** ORTEP drawing with 45% ellipsoid probability showing atom labeling of M(TAP)<sub>2</sub> (M = Cu(II) or Ni(II))

Figure 3 shows that the [N(CN)<sub>2</sub>]<sup>-</sup> ligand ion of the NaN(CN)<sub>2</sub> salt has been converted via in situ in the solvothermal reaction process to the TAP ligand. These changes can occur following the reaction mechanism for the formation of M(TAP)<sub>2</sub> described by Kopylovich *et al.* [11] The reaction mechanism for the formation of copper(II) 2,4-dimethoxy-1,3,5-triazapentadiene has been proposed by Kopylovich and Pombeiro,[1] wherein the reaction process of the formation of a compound [Cu(dca)<sub>2</sub>]<sub>n</sub>, which then occurs nucleophilic attack by methanol. Then one of the triple bonds of C ≡ N will be released and the N atom will carry the electron pair to form an amino bond of the H<sup>+</sup> of methanol. Meanwhile, the methoxy group (MeO), with a single pair of electrons, will bind to the C atom to form a C – OMe bond. The nucleophilic attack reaction process by methanol will continue on the other side of the C ≡ N group, in this process the NH group of the two 1,3,5-pentadiene ligands will form bonds with Cu<sup>2+</sup> metal ions to form complexes with bidentate ligands.

**Table 2.** Crystallographic data of the as-synthesized of M(TAP)<sub>2</sub> (M = Cu, Ni) complexes

Crystallography Data	The as-synthesized Cu(TAP) <sub>2</sub>	The as-synthesized Ni(TAP) <sub>2</sub>
Chemical formula	C <sub>8</sub> H <sub>16</sub> CuN <sub>6</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>16</sub> N <sub>6</sub> NiO <sub>4</sub>
Molecular weight	323.81 g mol <sup>-1</sup>	318.98 g mol <sup>-1</sup>
Temperature	296(2) K	293(2)K
Wavelength	0.71073 Å	0.71076 Å
Crystal lattice	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Lattice parameter	<i>a</i> = 10.0250(3) Å <i>b</i> = 5.6695(2) Å <i>c</i> = 11.6438(3) Å <i>α</i> = 90° <i>β</i> = 99.6960(10)° <i>γ</i> = 90°	<i>a</i> = 10.0011(9) Å <i>b</i> = 5.7512(3) Å <i>c</i> = 11.2619(10) Å <i>α</i> = 90° <i>β</i> = 98.301° <i>γ</i> = 90°
Volume	652.34(3) Å <sup>3</sup>	640.98(9) Å <sup>3</sup>
Z	2	4
Radiation source	Mo	Mo
F(000)	334	664
Density	1.649 g cm <sup>-3</sup>	3.305 g cm <sup>-3</sup>
Absorption coefficient	1.695 mm <sup>-1</sup>	3.070 mm <sup>-1</sup>
Data/restraints/parameter	1976 / 0 / 90	669 / 0 / 90
R indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> 1 = 0.0380; <i>wR</i> 2 = 0.0721	<i>R</i> 1 = 0.0290, <i>wR</i> 2 = 0.0654
R indices (all data)	<i>R</i> 1 = 0.0528; <i>wR</i> 2 = 0.0789	<i>R</i> 1 = 0.0327, <i>wR</i> 2 = 0.0680

The results of the refinement of crystallographic data using the Apex 4 program obtained a complex structure, as shown in Figure 3. The data in Table 2 shows that the crystals formed have the molecular formula  $MC_8H_{16}N_6$  ( $M = Cu$  and  $Ni$ ) with  $P21/n$  space groups and a monoclinic crystal system. The results obtained in the crystallographic data of this study are the same as the research conducted by Boc'a *et al.* [15] which synthesized  $Cu(TAP)_2$  and research by Andrusenko *et al.* [12] which synthesized  $Ni(TAP)_2$ .

The complex compound  $M(TAP)_2$  isostructural for the central ion  $Cu^{2+}$  and  $Ni^{2+}$ , crystallized in the  $P21/n$  space group showing the  $P$  lattice type, monoclinic crystal system, has 4 symmetries including glide plane, screw axis, identity, and center inversion. The symmetry operations used on molecules to produce equivalent atoms or molecules are (i)  $x, y, z$ ; (ii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $-x, -y, -z$ ; (iv)  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ . The center of symmetry lies on the central atom and causes the center of inversion to be at  $[0,0,0]$ . The screw axis occurs with 2 folds in the direction  $[0,1,0]$  in  $\frac{1}{4}, y, \frac{1}{4}$ , with the component  $[0,1/2,0]$ , which can be seen in Figure 4. The glide plane is perpendicular to  $[0,1,0]$  with the glide component  $[1/2, 0, 1/2]$ .

Data in Tables 3 and 4 indicate that the corners of the planar rectangle around the central atom show distortion due to the delocalization of negative charge on each  $N-C-N$  with delocalized  $\pi$  bonds: the bond lengths of 1.325 Å and 1.320 Å for  $Ni(TAP)_2$ , 1.335 Å and 1.326 Å for  $Cu(TAP)_2$  which are characters of  $C(sp^2)-N(sp^2)$ . The  $N3-C2$  and  $N2-C1$  bonds are 1.292 Å and 1.299 Å for  $Ni(TAP)_2$ , 1.293 Å and 1.298 Å for  $Cu(TAP)_2$ , which are characters of  $C(sp^2)=N$ . [16] From the bond length data, it can also be concluded that there is resonance in the compound. The resonance is proven by the bond length of  $C$  and  $N$  difference between  $C-N$  (1.465 Å) and  $C=N$  (1.279 Å). The square planar structure of  $Cu^{2+}$  and  $Ni^{2+}$  is also found in the  $[Cu(BTK)_2 \cdot H_2O]$  complex and copper(II) dimethylglyoxime ( $Cu(HD)_2$ ). [17], [18]

**Table 3.** The bond length and angles of the as-synthesized  $Cu(TAP)_2$

Bond length	Å	Bond Angle	Degree
Cu-N1	1.9471(19)	$N3^i-Cu-N3$	180
Cu-N2	1.9425(19)	$N1-Cu-N1^i$	180
N1-C1	1.293(3)	$N1-Cu-N3^i$	92.01(8)
N2-C2	1.326(3)	$N1^i-Cu-N3^i$	87.99(8)
N3-C2	1.298(3)	$N1^i-Cu-N3$	92.01(8)
N2-C1	1.335(3)	$N1-Cu-N3$	87.99(8)
C4-O2	1.436(3)		
C1-O1	1.367(2)		
C3-O1	1.438(3)		
C2-O2	1.352(2)		

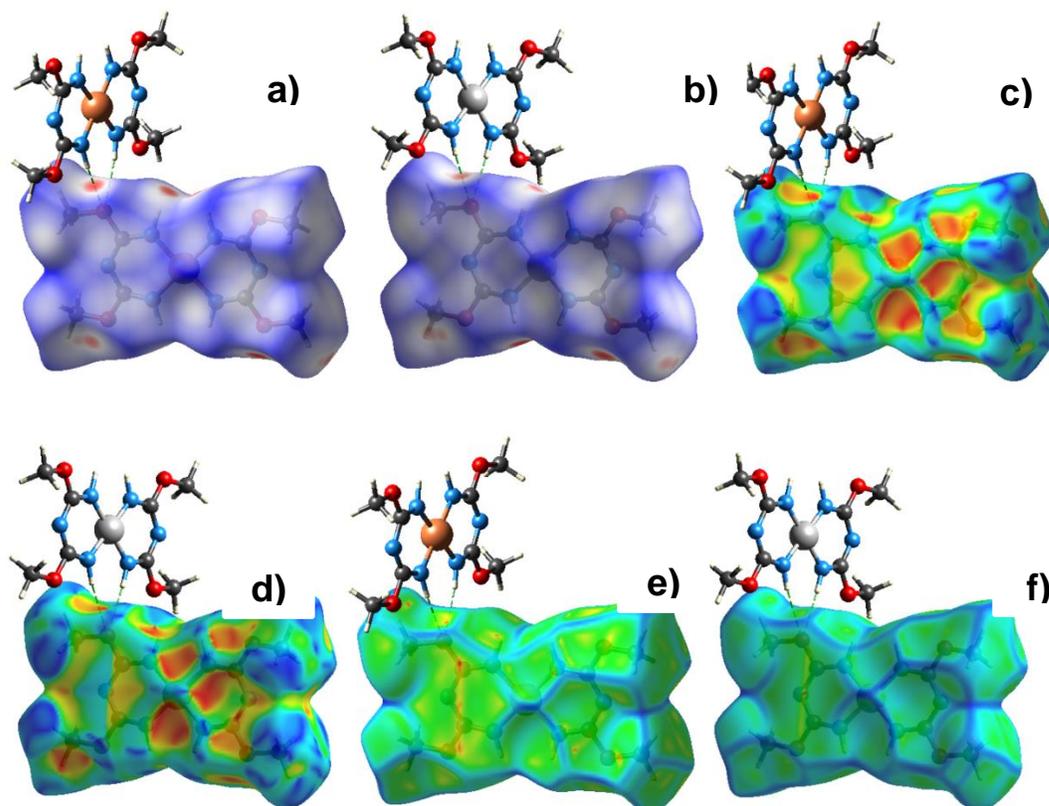
**Table 4.** The bond length and angles of the as-synthesized  $Ni(TAP)_2$

Bond length	Å	Bond Angle	Degree
Ni-N1	1.867(3)	$N3^i-Ni-N3$	180
Ni-N2	1.867(3)	$N1-Ni-N1^i$	180
N1-C1	1.299(4)	$N1-Ni-N3^i$	90.85(13)
N2-C2	1.320(5)	$N1^i-Ni-N3^i$	89.16(13)
N3-C2	1.292(4)	$N1^i-Ni-N3$	90.84(13)
N2-C1	1.325(5)	$N1-Ni-N3$	89.15(13)
C4-O2	1.442(5)		
C1-O1	1.357(4)		
C3-O1	1.429(5)		
C2-O2	1.364(4)		

## Hirshfeld Surface Analysis

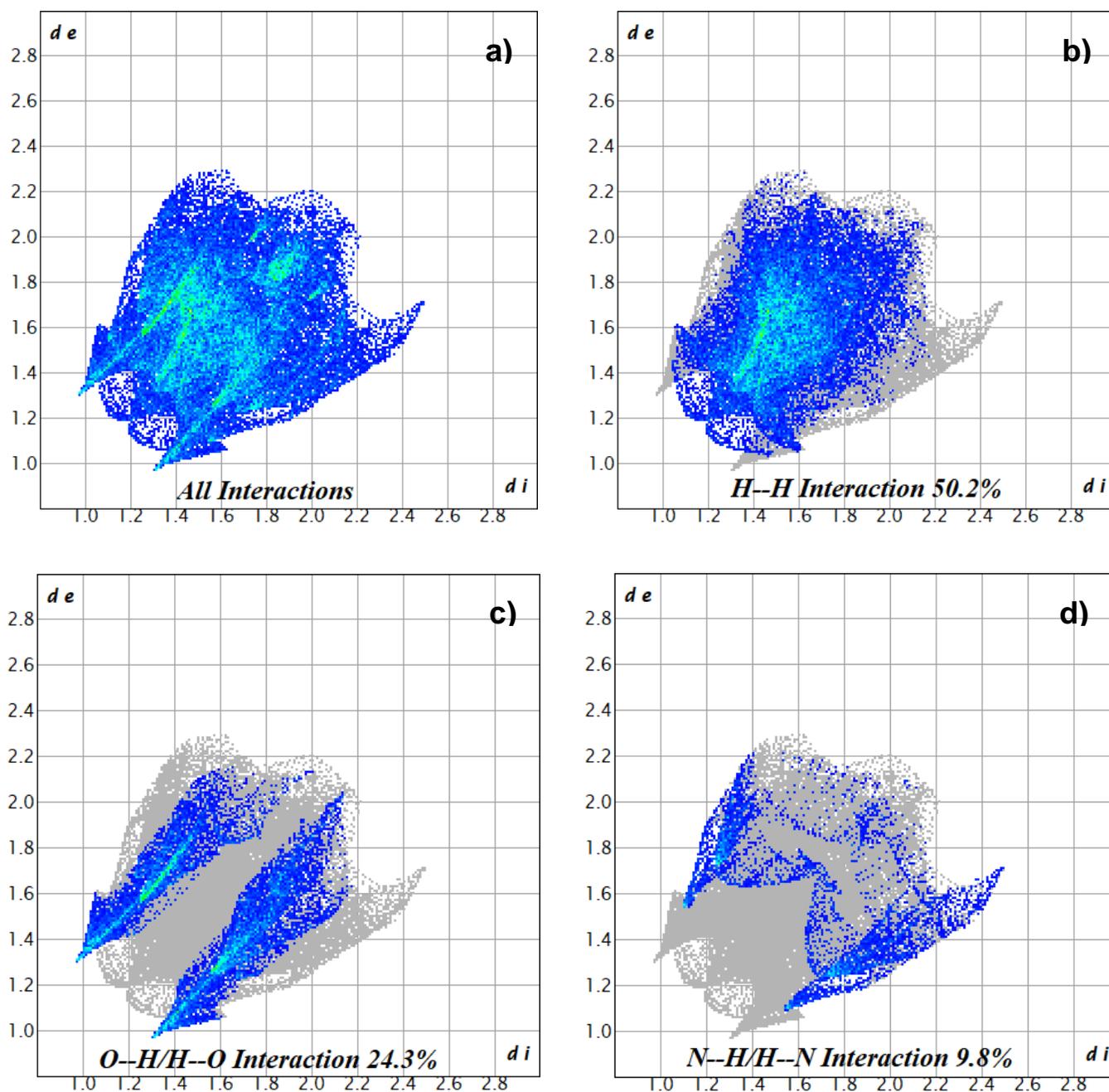
Hirshfeld surface analysis was used to measure and visualize intermolecular interaction in the crystal packing. 3D analysis of Hirshfeld surface over  $d_{norm}$  and 2D fingerprint plot were calculated using *CrystalExplorer* (Version 21.5). Hirshfeld surface of  $M(TAP)_2$  ( $M = Cu, Ni$ ) complex on Figure 4(a)-(b) plotted over  $d_{norm}$  in the range from -0.2324 to +1.2149 for  $Cu(TAP)_2$  and -0.2486 to +1.1452 for  $Ni(TAP)_2$ . Intermolecular interaction in the form of  $O-H-N$  hydrogen bond can be seen in the red

portion around O atom from methoxy group with amine group from neighboring molecule. The length of hydrogen bond O—H—N of were 2.524 Å for Cu(TAP)<sub>2</sub> and 2.426 Å for Ni(TAP)<sub>2</sub> measured with *Mercury2022.2.0* software. The shape index results in Figure 4(c)-(d) were showing a red part on O atom from methoxy group indicated as hydrogen bond donor, while the blue part around the amine group was the hydrogen bond acceptor. The curvedness analysis gives information about the flat proportion of the surface (green color) and the curved part (blue color), the result of Ni(TAP)<sub>2</sub> having more curvedness than Cu(TAP)<sub>2</sub> with greater blue color showing in the Hirshfeld surface in Figure 4(e)-(f).

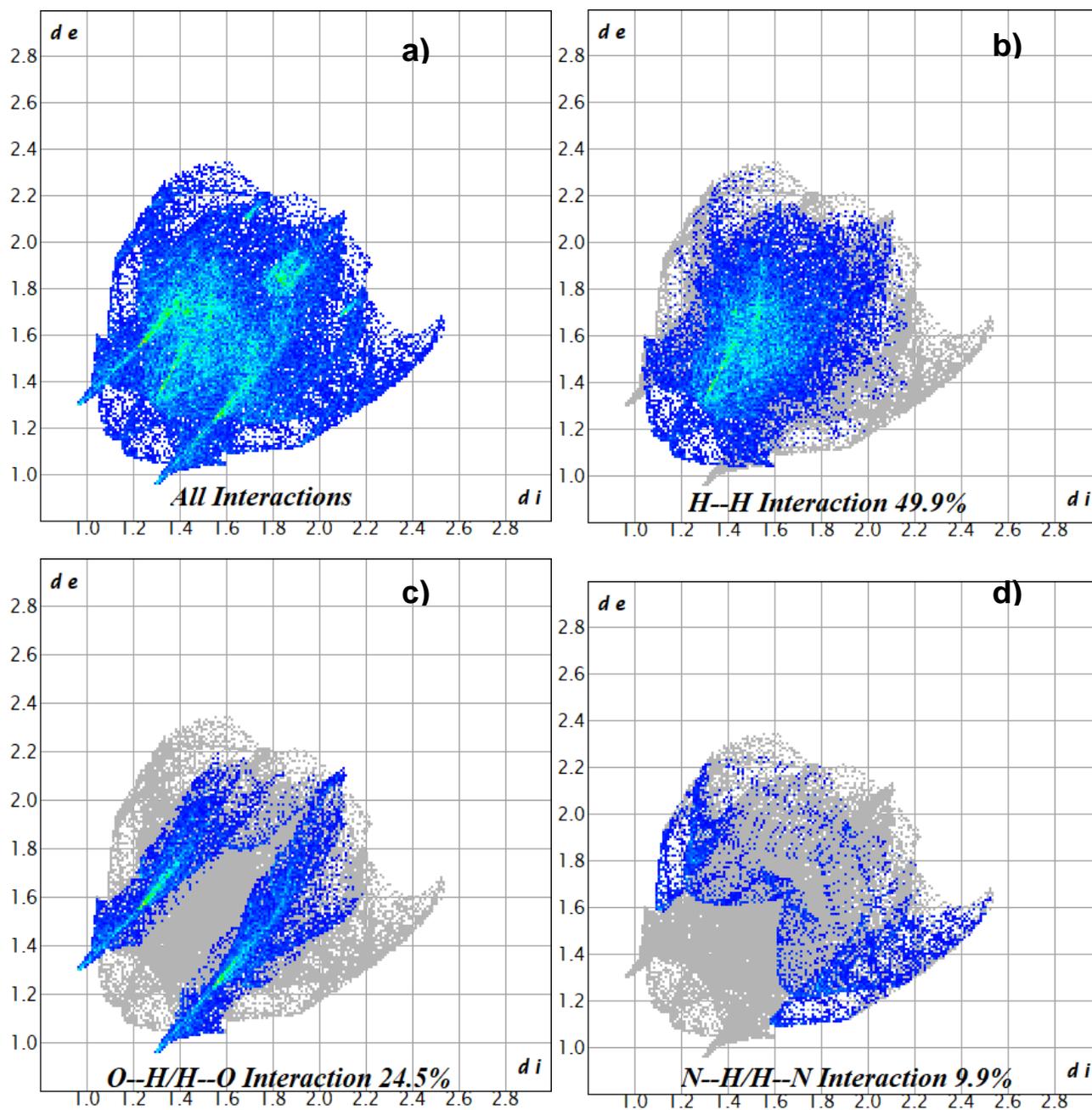


**Figure 4.** Hirshfeld Surface analysis (a)  $d_{\text{norm}}$  Cu(TAP)<sub>2</sub>, (b)  $d_{\text{norm}}$  Ni(TAP)<sub>2</sub>, (c) shape index Cu(TAP)<sub>2</sub>, (d) shape index Ni(TAP)<sub>2</sub>, (e) curvedness Cu(TAP)<sub>2</sub>, and (f) curvedness Ni(TAP)<sub>2</sub>

The overall 2D fingerprint plot for Cu(TAP)<sub>2</sub> [Figure 5(a)] and those contacts with the most contribution on Hirshfeld surface are H—H (50.2% contribution), O—H/H—O (24.3% contribution), and N—H/N—H (9.8% contribution) shown in Figure 5(b)-(d) respectively. The other contacts with minor contribution are from C—C (0.8% contribution), C—H/H—C (4.5% contribution), Cu—H/H—Cu (3.7% contribution), Cu—N/N—Cu (1.4% contribution), N—C/C—N (3.9% contribution), and N—N (1.4% contribution). 2D fingerprint plot for Ni(TAP)<sub>2</sub> in Figure 6 showing a similarity in term of shape and contacts that contributed as the effect of structure similarity by the two complexes. All interaction on Hirshfeld surface of Ni(TAP)<sub>2</sub> seen in Figure 6(a) with the most contribution come from H—H (49.9% contribution), O—H/H—O (24.5% contribution), and N—H/N—H (9.9% contribution) contacts. The other contacts except from those with minor contribution are C—C (1.3% contribution), C—H/H—C (4.8% contribution), Ni—H/H—Ni (3.6% contribution), Ni—N/N—Ni (1.1% contribution), N—C/C—N (3.1% contribution), and N—N (1.5% contribution). The intermolecular hydrogen bonding and van der Waals interactions playing major roles in the crystal packing of Cu(TAP)<sub>2</sub> and Ni(TAP)<sub>2</sub> can be seen in the large number of H—H, O—H/H—O, and N—H/N—H interactions in both of complexes, which is related to broad spectra peak at 3344 cm<sup>-1</sup> and 3331 cm<sup>-1</sup> for Cu(TAP)<sub>2</sub> and Ni(TAP)<sub>2</sub> respectively [19].



**Figure 5.** 2D fingerprint plots for Cu(TAP)<sub>2</sub>, showing (a) all interactions, (b) H—H interaction, (c) O—H/H—O interaction, and (d) N—H/H—N interaction.



**Figure 6.** 2D fingerprint plots for Ni(TAP)<sub>2</sub>, showing (a) all interactions, (b) H—H interaction, (c) O—H/H—O interaction, and (d) N—H/H—N interaction.

### Electrical Conductivity

Based on structural observations, the M(TAP)<sub>2</sub> complex is a molecular complex in which both ligands are bound to the central ion. However, it is necessary to test the stability of the complex in solution through an electrical conductivity test. If the complex solution can conduct electricity, then the ligands can dissociate in the solution. Complex compounds must be used as catalysts to be stable (not decomposed) in the solution. The measurement of electrical conductivity M(TAP)<sub>2</sub> is presented in Table 5.

**Table 5.** Solution conductivity of precursors and the as-synthesized complexes

Compounds	Solution Conductivity ( $\mu\text{S cm}^{-1}$ )
Methanol + DMSO	3.92
$\text{NaN}(\text{CN})_2$	1376
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	309
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	214
The as-synthesized $\text{Ni}(\text{TAP})_2$	36.7
The as-synthesized $\text{Cu}(\text{TAP})_2$	143.7

The copper(II) 2,4-dimethoxy-1,3,5-triazapentadiene compound could be categorized as an ionic complex if it is ionized in a solution and the electrical conductivity value produced is close to or greater than that of the  $\text{Cu}^{2+}$  salt or sodium dicyanamide. On the other hand, the compound could be categorized as a molecular complex if the electrical conductivity value produced is less than that of the other compounds. In this EC test, the complex compound was dissolved in methanol solvent and added with a few drops of DMSO. All tested materials were dissolved in a solvent mixture of DMSO and methanol. Compounds that can be dissolved into their constituent ions can conduct electricity, so the more compounds dissolved into ions in solution, the greater the electrical conductivity. The results of the EC test showed that the synthesized complex was a complex molecular compound because the electrical conductivity of the complex compound was lower than its metal salt and sodium dicyanamide.

**Table 6.** Atomic coordinate of  $\text{Cu}(\text{TAP})_2$  complex

No.	Label	Xfraction + ESD	Yfraction + ESD	Zfraction + ESD
1	Cu1	0.50000	0.0000	0.50000
2	O1	0.39309(16)	0.4733(3)	0.23019(14)
3	O2	0.80780(15)	0.4586(3)	0.45981(14)
4	N1	0.42033(19)	0.1854(4)	0.36500(17)
5	H1	0.341137	0.143416	0.330716
6	N2	0.66099(19)	0.1947(4)	0.50993(17)
7	H2	0.72533	0.165615	0.566929
8	N3	0.59646(18)	0.4562(3)	0.35124(16)
9	C1	0.4485(3)	0.6741(5)	0.1792(2)
10	H3	0.381763	0.737666	0.118237
11	H4	0.526688	0.626483	0.14752
12	H5	0.473935	0.792175	0.23792
13	C2	0.4737(2)	0.3650(4)	0.32135(18)
14	C3	0.6822(2)	0.3639(4)	0.44002(18)
15	C4	0.8384(3)	0.6395(5)	0.3819(2)
16	H6	0.932231	0.681619	0.401382
17	H7	0.783438	0.775658	0.388985
18	H8	0.819953	0.582139	0.303242
19	O1'	0.60691(16)	-0.4733(3)	0.76981(14)
20	O2'	0.19220(15)	-0.4586(3)	0.54019(14)
21	N1'	0.57967(19)	-0.1854(4)	0.63500(17)
22	H1'	0.658863	-0.14342	0.669284
23	N2'	0.33901(19)	-0.1947(4)	0.49007(17)
24	H2'	0.27467	-0.16562	0.433071
25	N3'	0.40354(18)	-0.4562(3)	0.64876(16)
26	C1'	0.5515(3)	-0.6741(5)	0.8208(2)
27	H3'	0.618237	-0.73767	0.881763
28	H4'	0.473312	-0.62648	0.85248
29	H5'	0.526065	-0.79218	0.76208
30	C2'	0.5263(2)	-0.3650(4)	0.67865(18)
31	C3'	0.3178(2)	-0.3639(4)	0.55998(18)
32	C4'	0.1616(3)	-0.6395(5)	0.6181(2)
33	H6'	0.067769	-0.68162	0.598618
34	H7'	0.216562	-0.77566	0.611015
35	H8'	0.180047	-0.58214	0.696758

**Table 7.** Atomic coordinate of Ni(TAP)<sub>2</sub> complex

No.	Label	Xfraction + ESD	Yfraction + ESD	Zfraction + ESD
1	Ni1	0.5000	0.0000	0.5000
2	O1	0.8052(2)	0.4442(4)	0.4623(2)
3	O2	0.3924(2)	0.4613(4)	0.2309(2)
4	N1	0.6550(3)	0.1841(5)	0.5106(3)
5	H1	0.71776	0.153912	0.569198
6	N2	0.4228(3)	0.1775(5)	0.3690(3)
7	H2	0.343485	0.136149	0.335933
8	N3	0.5967(3)	0.4447(5)	0.3493(3)
9	C1	0.8386(4)	0.6217(7)	0.3828(3)
10	H3	0.93208	0.663194	0.403484
11	H4	0.783229	0.755857	0.389762
12	H5	0.823083	0.565156	0.301779
13	C2	0.6790(4)	0.3526(6)	0.4398(3)
14	C3	0.4745(4)	0.3552(6)	0.3222(3)
15	C4	0.4466(4)	0.6619(7)	0.1776(4)
16	H6	0.378825	0.726639	0.117665
17	H7	0.523592	0.616387	0.141126
18	H8	0.473452	0.776106	0.238539
19	O1'	0.1948(2)	-0.4442(4)	0.5377(2)
20	O2'	0.6076(2)	-0.4613(4)	0.7691(2)
21	N1'	0.3450(3)	-0.1841(5)	0.4894(3)
22	H1'	0.28224	-0.15391	0.430802
23	N2'	0.5772(3)	-0.1775(5)	0.6310(3)
24	H2'	0.656515	-0.13615	0.664067
25	N3'	0.4033(3)	-0.4447(5)	0.6507(3)
26	C1'	0.1614(4)	-0.6217(7)	0.6172(3)
27	H3'	0.06792	-0.66319	0.596516
28	H4'	0.216771	-0.75586	0.610238
29	H5'	0.176917	-0.56516	0.698221
30	C2'	0.3210(4)	-0.3526(6)	0.5602(3)
31	C3'	0.5255(4)	-0.3552(6)	0.6778(3)
32	C4'	0.5534(4)	-0.6619(7)	0.8224(4)
33	H6'	0.621175	-0.72664	0.882335
34	H7'	0.476408	-0.61639	0.858874
35	H8'	0.526548	-0.77611	0.761461

## Conclusions

Our synthesis strategy efficiently produced the as-synthesized Cu(TAP)<sub>2</sub> and Ni(TAP)<sub>2</sub> because the TAP ligand was in-situ produced in the mother liquor reaction. Uniquely, the as-synthesized Cu(TAP)<sub>2</sub> was formed with and without CoCl<sub>2</sub> in the solution, and both crystals are isostructure. The as-synthesized Ni(TAP)<sub>2</sub> crystals were formed only with presenting ZnCl<sub>2</sub> in the mother liquor. All crystals were obtained directly during the solvothermal cooling and evaporation at room temperature. The as-synthesized crystals were needle-shaped purplish red crystals for Cu(TAP)<sub>2</sub> with a yield of 91% and needle-shaped orange crystals for Ni(TAP)<sub>2</sub> with a yield of 47%. The two crystals obtained have a monoclinic lattice type and a P21/n space group. In this study, their electrical conductivity of both crystal was tested, and by using Hirshfeld surface analysis intermolecular hydrogen interactions were found.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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