

Synthesis and Structure of Copper(II) Complexes with an Imine Derived from 4-nitroaniline and 2-hydroxy-1-naphthaldehyde

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THIS PAPER IS DEDICATED TO PROF. BRANKO KAITNER ON THE OCCASION OF HIS 80TH BIRTHDAY

Abstract: In this work, we have focused on the synthesis of a copper(II) complex with an imine derived from 4-nitroaniline (**4noa**) and 2-hydroxy-1-naphthaldehyde (**n**), as well as its coordinatively saturated adducts. The obtained metal complex is reasonably soluble in pyridine (**py**) and tetrahydrofuran (**thf**), resulting in the formation of two adducts. The complex and adducts have been synthesized both by conventional solvent-based methods and by liquid-assisted grinding (LAG). All products were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD). Their crystal and molecular structures were determined by single crystal X-ray diffraction (SCXRD). The complex crystallizes in the space group $P2_1/c$ with $a = 11.1022(5)$, $b = 9.4550(5)$, $c = 13.7613(7)$ Å and $\beta = 94.035(4)^\circ$. Both adducts crystallize in the space group $P\bar{1}$ with the following lattice parameters: **py** adduct, $a = 9.1696(6)$ Å, $b = 9.4808(9)$ Å, $c = 11.6801(8)$ Å, $\alpha = 93.300(7)^\circ$, $\beta = 108.738(6)^\circ$, $\gamma = 100.650(7)^\circ$; and **thf** adduct, $a = 9.1721(13)$ Å, $b = 9.5797(13)$ Å, $c = 11.4448(15)$ Å, $\alpha = 96.138(11)^\circ$, $\beta = 106.466(12)^\circ$, $\gamma = 101.543(12)^\circ$.

Keywords: imine copper(II) complex, adducts, solution synthesis, mechanochemical synthesis, *one-pot* mechanochemical synthesis, crystal structure.

INTRODUCTION

A VAST number of structural studies on imines^[1] derived from hydroxyaryl aldehydes and their coordination compounds have been undertaken in the last five decades.^[2–5] They have become some of the most typical ligands for coordinating transition and inner transition metal ions.^[6–9] This most commonly involves imine ligands derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde.^[10–16] Imine metal complexes are mainly investigated due to their applications in catalysis,^[17,18] pigment chemistry^[19,20] and optical materials.^[21] There are also a number of investigations on imine transition metal complexes which showed that such compounds possess biological activity, such as anticancer, antimicrobial, anti-inflammatory, *etc.*^[22–30] More recently, coordination compounds of imines also started drawing attention in mechanochemical synthesis^[31,32] as well as in synthesis of multi component crystals, particularly halogen-bonded

cocrystals.^[33–35] From the point of view of crystal engineering these compounds can be designed to produce suitable building blocks for further connection into desired and designed supramolecular architectures. In order to produce such metal-organic crystal materials, the first step is the selection of functionalized imines with pendant acceptor groups that can participate in non-bonding interactions such as halogen and hydrogen bonds.^[33–39] The next challenging step is making adducts by binding additional molecules that can act as bridging ligands, forming coordination polymers, or that can be employed to place functional groups which can participate in supramolecular interactions on the periphery of metal-organic complexes.^[40–46]

A search of the Cambridge Structural Database^[47] for transition metal imine complexes, where imines are formed from a general *o*-hydroxy aromatic aldehyde and an aniline or aniline derivative, resulted in 1587 entries. Of those, 365 entries correspond to copper(II) imine

complexes, of which only 14 correspond to adducts formed with either pyridine, *N,N*-dimethylformamide, dimethyl sulfoxide, acetonitrile or water. 41 entry corresponds to complexes with imines derived from 2-hydroxy-1-naphthaldehyde and aromatic amines that have peripherally located various groups such as: dimethylamino, acetyl, butyl, methyl, phenoxy groups or halogen atoms. The ligands display a wide range of geometric arrangements around the Cu(II) ion, mostly going from the ideal trans-square planar structure to deformed tetrahedral geometry.

In this work, the main goal was to prepare a square planar copper(II) complex with an imine ligand, **n4noa**, derived from 2-hydroxy-1-naphthaldehyde (**n**) and 4-nitroaniline (**4noa**), Figure 1, as well as its adducts with pyridine and tetrahydrofuran. The choice of the type of imine that has peripherally located nitro groups allowed us to study supramolecular bonding motifs and geometries that imine ligands have, both in the pure complex and in the obtained adducts. Pyridine and tetrahydrofuran were selected because they would not enable the formation of polymers and because they are reliable monodentate ligands.^[47] We were inspired to pursue the solvent-free mechanochemical experiments in our study by previous reports on mechanochemical synthesis of coordination compounds.^[48–52] Over the past two decades mechanochemical methods such as liquid-assisted grinding (LAG)^[53,54] or ion- and liquid-assisted grinding (ILAG)^[55] have shown great potential for efficient, clean and environmentally friendly preparation of new materials, in both supramolecular and covalent synthesis.^[56–60] Also, earlier reports on multi-step and one-pot multi-component synthesis by grinding^[34,61,62] have demonstrated the attractive prospect of extending the advantages of mechanochemistry to the synthetic procedure, most importantly the ability to synthesize complex products rapidly from the simplest possible precursors.

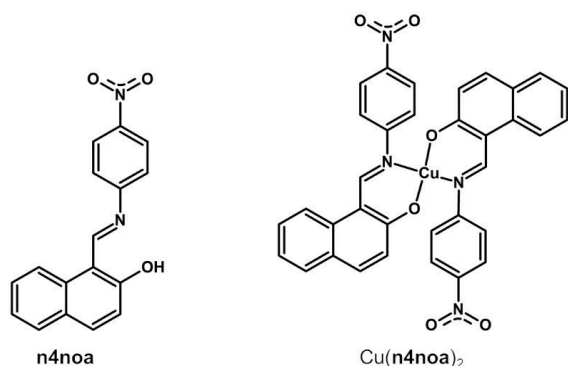


Figure 1. The imine ligand, **n4noa**, and the unsaturated copper(II) complex, $\text{Cu}(\text{n4noa})_2$.

EXPERIMENTAL

2-hydroxy-1-naphthaldehyde and 4-nitroaniline were purchased from Aldrich. Copper(II) acetate monohydrate (**CuOAc**) was purchased from Acros Organics. Acetonitrile was purchased from J. T. Baker. Methanol was purchased from Carlo Erba. Dichloromethane was purchased from Alkaloid. All solvents were used without further purification.

Mechanochemical syntheses of the complex and the adducts were conducted in a Retsch MM200 ball mill operating at 25 Hz frequency using Form-Tech Scientific SmartSnap stainless steel jars along with stainless steel balls 7 mm in diameter. All syntheses were repeated to ensure reproducibility.

The products obtained by solution-based and mechanochemical synthesis experiments were characterized by powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction (SCXRD) experiments.

PXRD experiments were performed on a PHILIPS PW 1840 X-ray diffractometer with $\text{CuK}\alpha_1$ (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 3 to 40° (2θ) with a continuous step size of 0.03°, and measuring time of 0.3 s per step. Data collection and analysis were performed using the program package Philips X'Pert.^[63]

SCXRD experiments were performed at 295 K on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire3 CCD detector, using graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation. Programs CrysAlis CCD and CrysAlis RED were used for data collection, cell refinement and data reduction.^[64] All structures were solved and refined using the SHELXT and SHELXL programs, respectively.^[65–67] Structural refinement was performed on F^2 using all data. All alkyl and aryl hydrogen atoms were placed at calculated positions and treated as riding on their parent atoms. All calculations were performed using the WinGX crystallographic suite of programs.^[68] The molecular structures of compounds and their molecular packing projections were prepared by Mercury.^[69]

Thermal studies (TGA-SDTA) were performed on a Mettler Toledo TGA/SDTA851 instrument using aluminium crucibles under an N_2 atmosphere and in the temperature range of 25–500 °C (heating rate, 10 °C min^{-1}).

Solution Synthesis and Single Crystal Preparation

Synthesis of imine, **n4noa**

The imine derived from 2-hydroxy-1-naphthaldehyde (**n**) and 4-nitroaniline (**4noa**), *N*-(4-nitrophenyl)-2-hydroxy-1-naphthaldehyde, was prepared by a conventional solvent-based method. A solution of **n** (1.73 g, 10.0 mmol) in

35.0 mL of hot methanol was filtered into a solution of **4noa** (1,38 g, 10.0 mmol) in 35.0 mL of hot methanol. The resultant mixture was left at room temperature, and, after 2 hours, a red-brown product formed and was filtered at lowered pressure over a Büchner funnel. The identity of the obtained product was confirmed by comparing its X-ray powder pattern to that calculated from entry EVINOM obtained from the Cambridge Structural Database.^[43] Yield: 55.5 %.

Synthesis of $\text{Cu}(\text{n4noa})_2$

CuOAc (200.0 mg, 1.00 mmol) and **n4noa** (584.6 mg, 2.00 mmol) were mixed with 40.0 mL of methanol and 40.0 mL of acetonitrile in a round flask and stirred while heating under reflux for 3.0 h. The precipitate changes color into dark brown. Yield: 76.3 %. Single crystals of $\text{Cu}(\text{n4noa})_2$ were prepared by dissolving of 10.0 mg of $\text{Cu}(\text{n4noa})_2$ in 15.0 mL of hot dichloromethane. The mixture was left to evaporate slowly at room temperature. Single crystals were isolated after three days.

Synthesis of $\text{Cu}(\text{n4noa})_2(\text{thf})_2$

10.0 mg of $\text{Cu}(\text{n4noa})_2$ was dissolved in 15 mL of hot **thf**, with thorough shaking and reheating of the mixture in order to prevent the solution from boiling out of the crystallization vessel. The mixture was left to crystallize at room temperature. A few single crystals and bulk material were isolated after three days. A PXRD comparison of the bulk material with $\text{Cu}(\text{n4noa})_2(\text{thf})_2$ single crystals ground into a powder revealed the complete conversion of the $\text{Cu}(\text{n4noa})_2$ complex into the **thf** adduct.

Synthesis of $\text{Cu}(\text{n4noa})_2(\text{py})_2$

20.0 mg of $\text{Cu}(\text{n4noa})_2$ was dissolved in 5 mL of hot **py**, with thorough shaking and reheating of the mixture in order to prevent the solution from boiling out of the crystallization vessel. The mixture was left to crystallize at room temperature. A few single crystals and bulk material were isolated after a week. A PXRD comparison of the bulk material with $\text{Cu}(\text{n4noa})_2(\text{py})_2$ single crystals ground into a powder revealed the complete conversion of the $\text{Cu}(\text{n4noa})_2$ complex into the **py** adduct.

Mechanochemical Synthesis

LAG synthesis of $\text{Cu}(\text{n4noa})_2$

A mixture of **CuOAc** (12.5 mg, 62.6 mmol) and **n4noa** (36.6 mg, 125.2 mmol) was placed in a 10 mL stainless steel jar along with 15.5 μL of **thf** (or the same amount of acetonitrile or nitromethane) and two stainless steel balls 7 mm in diameter. The mixture was then milled for 30 minutes.

LAG synthesis of $\text{Cu}(\text{n4noa})_2(\text{py})_2$

The bulk material (reflux product) corresponding to the pure $\text{Cu}(\text{n4noa})_2$ complex (49.9 mg, 76.9 mmol) was placed

in a 10 mL stainless steel jar, along with 15.5 μL (195.9 mmol) of **py** and two stainless steel balls 7 mm in diameter. The mixture was then milled for 30 minutes.

One-pot LAG synthesis of $\text{Cu}(\text{n4noa})_2(\text{py})_2$

A mixture of **CuOAc** (12.5 mg, 62.6 mmol) and **n4noa** (36.6 mg, 125.2 mmol) was placed in a 10 mL stainless steel jar, along with 15.5 μL of **py** (195.9 mmol), 10.0 μL of triethylamine and two stainless steel balls 7 mm in diameter. The mixture was then milled for 45 minutes.

RESULTS AND DISCUSSION

The $\text{Cu}(\text{n4noa})_2$ complex was synthesized by reflux heating of a stoichiometric mixture of **CuOAc** and **n4noa** in a mixture of acetonitrile and methanol. The bulk product of the reflux heating experiment was recrystallized from a large volume of dichloromethane in order to obtain usable single crystals for SCXRD. Single crystals of the $\text{Cu}(\text{n4noa})_2(\text{py})_2$ and $\text{Cu}(\text{n4noa})_2(\text{thf})_2$ products were obtained by recrystallization of the bulk product from **py** or **thf**, respectively (Figure 2). All obtained products were identified by comparing their PXRD patterns with those calculated from single crystal data.

After we successfully synthesized and isolated the $\text{Cu}(\text{n4noa})_2$ complex by conventional solution-based methods, we attempted to synthesize it by grinding. First, we performed neat grinding (NG) of a mixture of **CuOAc** and **n4noa** mixture in a 1:2 stoichiometric ratio. After 60 minutes of ball milling, the reaction resulted in a mixture of

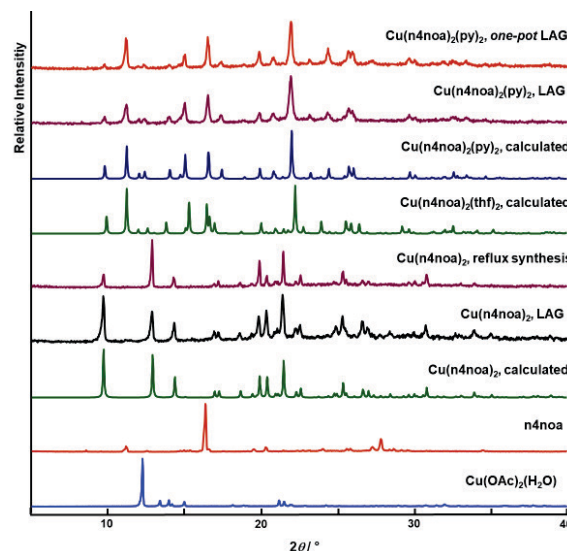


Figure 2. A comparison of X-ray diffraction patterns of reactants, products experimentally obtained by mechanochemical or solution-based methods and patterns calculated from single crystal data.

reactants. On the other hand, liquid-assisted grinding for 30 minutes with a small addition of **thf** (15.5 μL) led to the formation of $\text{Cu}(\mathbf{n4noa})_2$. As revealed by PXRD, this experiment provided the same product, $\text{Cu}(\mathbf{n4noa})_2$, as did the reflux and crystallization experiments (Figure 2). Next, we pursued mechanochemical synthesis of adducts previously prepared by the solution method. The $\text{Cu}(\mathbf{n4noa})_2$ bulk was mixed with a slight excess of **py** compared to the amount required by stoichiometry. The reaction was quantitative and pure $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ adduct was obtained after 30 minutes of grinding. A variety of experimental parameters have been tested for obtaining the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ adduct by grinding $\text{Cu}(\mathbf{n4noa})_2$ with **thf** (see the ESI, Table S2), but the desired product was not obtained. Next, we attempted to simplify the mechanochemical procedure by milling **CuOAc**, **n4noa** and **py** in a 1:2:2 stoichiometric ratio, with a small addition (10.0 μL) of triethylamine. As evidenced by PXRD, this one-pot approach quantitatively gave $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ after 30 min of LAG (Figure 2).

The TG curve of $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ (Figure S9) shows a mass loss of 9.1 % in the first decomposition step (onset at 256 $^\circ\text{C}$) which corresponds to a loss of approximately one **py** molecule from the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ adduct (expected for one **py** ligand is 9.9 %). The first decomposition step is followed by continuous mass loss. In case of the TG curve of $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ (Figure S10), a small step (2.1 % mass) probably corresponding to loss of adsorbed **thf** is followed by a bigger step with mass loss of 10.6 % in the range between

220 and 300 $^\circ\text{C}$ (onset at 255 $^\circ\text{C}$) which corresponds to a loss of approximately one **thf** molecule from the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ adduct (expected for one **thf** ligand is 9.1 %). This decomposition step is closely followed by continuous mass loss.

Single crystal X-ray diffraction revealed that $\text{Cu}(\mathbf{n4noa})_2$ crystallizes in the $P2_1/c$ space group, while both adducts crystallize in the $P\bar{1}$ space group. All three compounds have C_i symmetry. The Cu(II) metal center of $\text{Cu}(\mathbf{n4noa})_2$ is coordinated by two bidentate **n4noa** ligands, and has square planar coordination geometry (Figure 3a). Upon addition of two adduct molecules in either $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ or $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$, the metal center has octahedral coordination geometry. Pyridine molecules in the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ adduct are connected to the central copper(II) ion through the pyridine nitrogen atom (Figure 3b), and in the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ adduct, **thf** molecules are connected to the central copper(II) ion through the tetrahydrofuran oxygen atom ($d(\text{N3}_{\text{py}} - \text{Cu}) = 2.605(5)$ \AA , $d(\text{O2}_{\text{thf}} - \text{Cu}) = 2.600(8)$ \AA) (Figure 3c). The elongation of metal-ligand bonds in hexacoordinated metal complexes is a common example of one type of Jahn-Teller effect present in copper(II) compounds.^[70–72] For example, a search of the Cambridge Structural Database for hexacoordinated copper complexes coordinated by nitrogen or oxygen atoms resulted in 10885 entries, of which 900 correspond to compounds where two of the copper–ligand distances are more than 2.6 \AA .^[47] Among these, the most entries feature a copper–ligand distance of 2.6–2.7 \AA , which is in excellent agreement with our results.

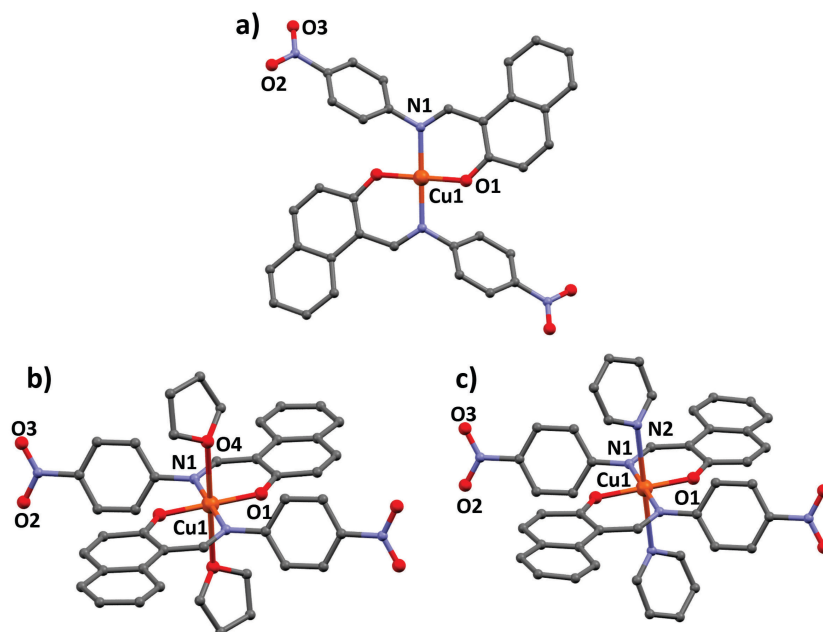


Figure 3. Molecular structures of the: a) $\text{Cu}(\mathbf{n4noa})_2$ complex, b) $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ adduct and c) $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ adduct. Hydrogen atoms are omitted for clarity.

The “bite” distance O...N between coordinated atoms of one chelate ligand molecule is slightly shorter in the pure complex when compared to the adducts. There is no significant difference in the Cu–O1 distance, but the Cu–N1 distance is elongated in adducts (Table S3). The ligand itself is not planar, due to the twist of the nitroaniline ring connected to the amino nitrogen out of the naphthalene moiety plane with the corresponding dihedral angles which are different in the adducts compared to that in complex because of the steric effects of adduct molecules and changes in the molecular environment and packing in the crystal. Spatial orientation of the *N*-substituent fragment (**noa**) changes between adducts and the complex. The angle between **noa** and **n** (2-hydroxy-1-naphthaldehyde fragment) aromatic ring planes is 44.2° in the

Cu(**n4noa**)₂ complex. In Cu(**n4noa**)₂(**thf**)₂ that angle is 68.2°, while in Cu(**n4noa**)₂(**py**)₂ it is 67.8°.

The crystal structure of the Cu(**n4noa**)₂ complex reveals that each molecule is connected *via* a pair of weak C–H...O hydrogen bonds to four adjoining molecules, thus leading to the formation of a 3D network (Figure 4a). One of the hydrogen bonds in a pair is formed between a nitroaniline fragment (as a C–H donor) of one complex molecule and a coordinated oxygen atom of the neighbouring complex molecule ($d(\text{C14}\cdots\text{O1}) = 3.308(5) \text{ \AA}$, $\angle(\text{C14-H14}\cdots\text{O1}) = 151.7^\circ$) and the other one is between the same nitroaniline fragment (as a C–H donor) and a nitro-group oxygen atom of another adjacent metal complex molecule ($d(\text{C13}\cdots\text{O2}) = 3.487(5) \text{ \AA}$, $\angle(\text{C13-H13}\cdots\text{O2}) = 153.2^\circ$).

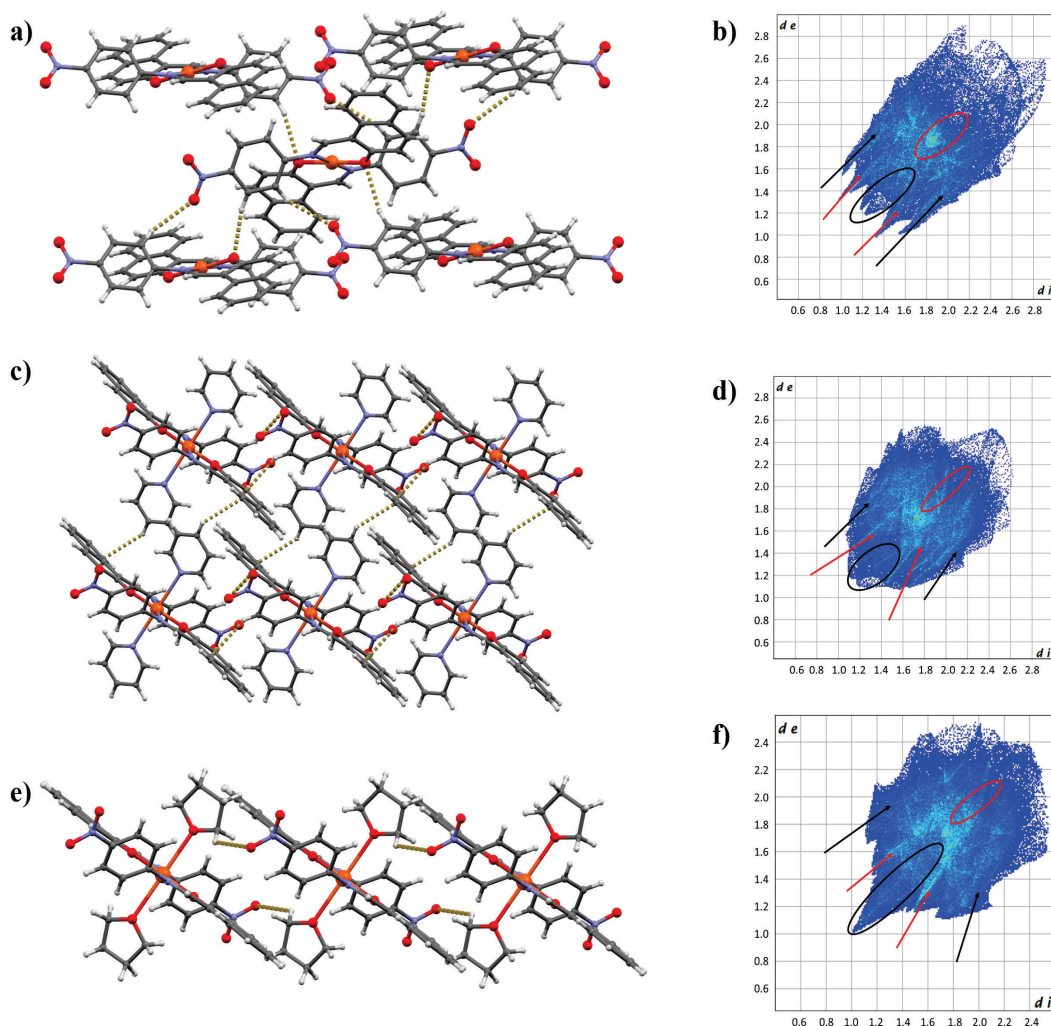


Figure 4. Interconnection of the subunits and the corresponding two-dimensional Hirshfeld surface fingerprint plots in the Cu(**n4noa**)₂ complex (a and b), Cu(**n4noa**)₂(**py**)₂ adduct (c and d) and the Cu(**n4noa**)₂(**thf**)₂ adduct (e and f). Regions on the fingerprint plots are marked as follows: red arrows for C–H...O contacts, black arrows for C–H...π contacts, red circle for C...C and black circle for short H...H contacts.

The formation of **py** and **thf** adducts reduces the interconnection capabilities of the metal complex. In the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$ crystal structure, a chain is formed where each adduct molecule is connected to two adjacent molecules *via* weak C–H...O contacts (Figure 4e) between **thf** and a nitro-group oxygen atom from an adjacent molecule ($d(\text{C}\cdots\text{O}) = 3.33(1) \text{ \AA}$, $\angle(\text{C}\cdots\text{H}\cdots\text{O}) = 125.6^\circ$). The chains are further connected into a layer by π -stacking of aromatic rings of naphthaldehyde fragments ($d(\text{C}\cdots\text{C}) = 3.34(1) \text{ \AA}$). In the $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$ crystal structure, metal-organic subunits are connected into layers *via* weak C–H... π contacts (Figure 4c) between **py** and **n** and **noa** and **n** ($d(\text{C}_{\text{py}}\cdots\text{C}_{\text{n}}) = 3.47(1) \text{ \AA}$, $d(\text{C}_{\text{noa}}\cdots\text{C}_{\text{n}}) = 3.719(7) \text{ \AA}$).

Hirshfeld surface analysis for all three compounds showed that the amount of C–H...O supramolecular contacts stays more or less the same throughout the series, as it is 22.7 % of the surface in $\text{Cu}(\mathbf{n4noa})_2$, 21.3 % in $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$, and 21.8 % in $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$. The amount of C...C contacts is reduced upon addition of **py** or **thf** ligands to the pure complex, as expected, going from 3.9 % to 1.5 % for the **py** adduct or 1.1 % for the **thf** adduct. The same trend was observed for C–H...C contacts, which include C–H... π contacts. The amount goes down from 32.7 % in the pure complex to 30.3 % for the **py** adduct or 24.1 % for the **thf** adduct. This conforms well to the fact that the **py** ligand is a π system, unlike the **thf** ligand. The reductions in the amounts of these supramolecular contacts are paralleled by a significant increase in the amount of H...H contacts, going from 30.7 % in the pure complex up to 42.2 % in the **py** adduct or 48.1 % in the **thf** adduct, which is again expected since these ligands feature additional peripherally located hydrogen atoms. The fingerprint plots of the three compounds (Figures 4b, 4d and 4f) are quite dissimilar, and the above mentioned trends going from the pure complex to adducts can be visualized. The parts corresponding to C–H...O and C–H... π get "pushed back" to higher values of d_e and d_i , indicating a change to significantly weaker supramolecular contacts, while the central part corresponding to H...H contacts becomes more prominent and is shifted towards lower d_e and d_i values.

CONCLUSION

To conclude, we have synthesized a coordinatively unsaturated square planar copper(II) complex with an imine ligand that has peripherally located nitro groups, and two of its octahedral adducts, one with **py** and the other with **thf** ligand molecules. The $\text{Cu}(\mathbf{n4noa})_2$ complex was successfully synthesized both from solution and by mechanochemical methods. Two adducts of the complex, with either **py** or **thf**, were also synthesized by solution-

based methods, although only one, $\text{Cu}(\mathbf{n4noa})_2(\mathbf{py})_2$, was successfully synthesized by mechanochemical means, both by milling the metal complex with pyridine and by *one-pot* synthesis. A number of mechanochemical experimental attempts were made to synthesize $\text{Cu}(\mathbf{n4noa})_2(\mathbf{thf})_2$, varying milling energy (through using milling balls of different sizes and therefore weight), milling time, addition of liquids (acetone, triethylamine and nitromethane) as potential templating agents, amount of **thf**, and swapping from milling the metal complex with **thf** to mixing copper(II) acetate, **n4noa** and **thf** in a *one-pot* mechanochemical method, but all of these experiments resulted in the formation of pure $\text{Cu}(\mathbf{n4noa})_2$. This is a somewhat unusual result, because mechanochemical methods are for the most part superior to commonly used solution-based methods (except slurry experiments) when it comes to scanning the possibility of forming new phases or products by simple supramolecular interactions. Thermal analysis has shown that the adducts are stable up to 255 °C, after which each of them features an almost continuous decomposition process in which the first step can be ascribed to the loss of **py** or **thf** ligand molecules.

While both the pure complex and adducts have unblocked peripheral nitro groups that are available for potential supramolecular interactions, the addition of ligand molecules and their spatial requirements results in the "pushing back" of the adjacent adduct molecules, which in turn leads to the lengthening of C–H...O contacts and the lessening influence of C...C contacts (due to movement of the naphthaldehyde fragment π systems away from their ideal stacking positions in the pure complex). Additionally, the insertion of ligand molecules twists the imine nitroaniline fragment away from the plane of the naphthaldehyde fragment again due to both spatial reasons (a perpendicular orientation would give the most space) and repulsion between the ligand and nitroaniline hydrogen atoms. These effects are best visible in the Hirshfeld surface fingerprint plots, where H...H contacts become more prominent at short contact distances over the above mentioned contact types.

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Supplementary Information. Electronic supplementary information (ESI) available and attached to the electronic version of the article at: <https://doi.org/10.5562/cca3992>: mechanochemical experiment details, PXRD patterns, TG data and crystal structure data. CCDC 2258450–2258452 contain crystallographic data for this paper.

PDF files with attached documents are best viewed with Adobe Acrobat Reader which is free and can be downloaded from [Adobe's web site](https://www.adobe.com).

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