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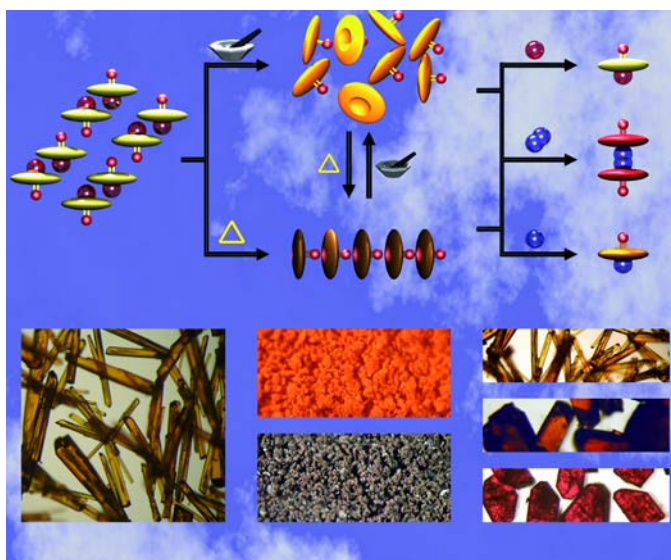


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PAPER

Schiff base derived from 2-hydroxy-1-naphthaldehyde and liquid-assisted mechanochemical synthesis of its isostructural Cu(II) and Co(II) complexes†

Dominik Cinčić* and Branko Kaitner

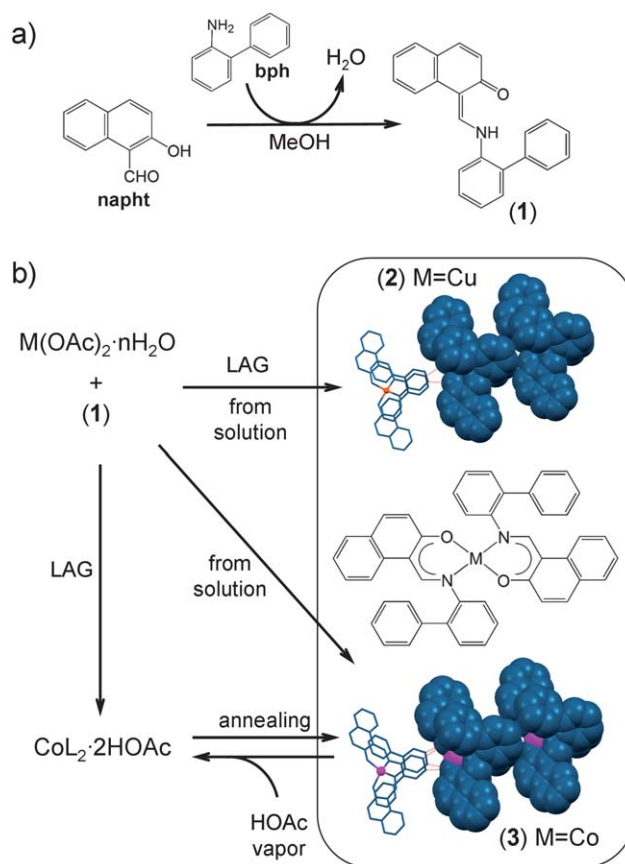
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The Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde, namely 1-[(2-biphenylamino)methylen]naphthalen-2(1*H*)-one (**1**) and its corresponding Cu(II) and Co(II) complexes (**2** and **3**, respectively) were synthesized and characterised by means of IR spectroscopy, thermal analysis and also by powder and single crystal X-ray diffraction. The mononuclear complexes have been obtained by a conventional solution-based method as well as by a mechanochemical method, *i.e.* by liquid-assisted grinding. The molecule of **1** is not planar and the keto-amino tautomer was detected from the molecular geometry consideration. The discrete molecules are π -stacked in the [100] direction and connected by weak intermolecular interactions. Compounds **2** and **3** are isostructural. The form of the copper atom coordination polyhedron is irregular square planar while the form of the cobalt atom coordination polyhedron is irregular tetrahedral. Both complexes form 1D chains in the [010] direction by weak C–H \cdots O and C–H \cdots C interactions.

Introduction

N-substituted imines, also known as Schiff bases, have been used extensively as ligands in the field of coordination chemistry for over a century, and in that time they have become some of the most typical ligands.¹ Particularly, a large number of transition metal complexes of Schiff-base ligands derived from the condensation of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with various primary amines have become the topics of contemporary research.^{2,3} These Schiff-base ligands may act as bidentate *N,O*-, tridentate *N,O,O*-, *N,O,N*-, *N,O,S*-, tetradentate *N,N,O,O*-donor ligands, *etc.*, which can be designed to yield mononuclear or binuclear complexes or one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) metal-organic frameworks.⁴ During the past decades there has been continuous interest in bis-bidentate Schiff base Cu(II) complexes and aldimine compounds derived from salicylaldehyde and 2-hydroxy-1-naphthaldehyde because in the solid state the ligands display a wide range of geometric arrangements around the metal ion, going from the ideal *trans*-square planar structure to a deformed tetrahedral geometry.²



Scheme 1 Summary of reactions to form coordination compounds.

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Altogether 48 entries corresponding to copper(II) coordination compounds exhibiting a bidentate *N,O*-donor ligand derived from 2-hydroxy-1-naphthaldehyde were found in the Cambridge Structural Database.² Only 18 ligands of them have been derived by condensation with aromatic amines. However, with the same search motifs for cobalt(II) coordination compounds, only 13 data sets were found with the ligands derived from 2-hydroxy-1-naphthaldehyde, and there are no cobalt(II) complexes exhibiting Schiff base with an aromatic *N*-substituent.

In this paper we report the rapid synthesis of mononuclear Cu(II) and Co(II) complexes from metal acetates (Scheme 1) *via* liquid-assisted grinding (LAG), *i.e.* by grinding in the presence of a small quantity of liquid phase.⁵ This is a mechanochemical method⁶ recently developed for the synthesis of molecular cocrystals held together by hydrogen- or halogen-bonding interactions.⁷ Mechanochemical synthesis is actually faster and more convenient than the conventional solvent-based methods. It has a significant potential in that sense, as it avoids large quantities of solvent and high temperatures, the method is easily manipulated and sometimes gives products that are different from those produced by solution reaction.⁸ Recent reports have shown that solvent-free synthesis and mechanochemistry are effective for the efficient and rapid synthesis of a wide range of metal complexes, which vary from mononuclear complexes to supramolecular materials, coordination networks, polymers and metal-organic frameworks (MOFs).^{9–11} Recently, Kuroda's group described annealing-assisted mechanochemical reactions as a useful and effective technique in the synthesis of coordination compounds. The heating process exhibits a variety of effects: the activation of discrete molecules by losing weakly coordinated ligands to form an activated complex or the rearrangement and diffusion of discrete molecules to form new crystals.¹⁰

In this paper, as a model of a *N,O*-ligand we targeted Schiff base obtained by condensation of 2-hydroxy-1-naphthaldehyde (**naph**) with 2-aminobiphenyl (**bph**) (Scheme 1). LAG is expected to result in ligand exchange reaction, in the loss of acetic acid and water and the formation of metal-nitrogen/oxygen coordination bonds. Because of the lack of hydrogen-bonding functionalities on the *N*-substituent the discrete units of coordination compounds are expected to self-assemble through potential weak intermolecular forces.

Results and discussion

Neat grinding of **1** with metal acetates in a stoichiometric ratio did not result in a reaction in the case of copper acetate but partial reaction with cobalt acetate was observed, as evidenced by PXRD. Guided by the observation that small amounts of a liquid phase can significantly enhance the scope and rate of mechanosynthesis we turned to LAG. Addition of a small quantity of triethylamine to the reaction mixtures, followed by grinding for 50 min, quantitatively provided new materials that were characterised by FT-IR spectroscopy, PXRD and TG, as described below. To observe LAG mechanosynthesis, as well as to facilitate the characterisation of new materials by single-crystal X-ray diffraction, LAG experiments were accompanied by conventional solution-based experiments. Both complex compounds, **2** and **3** were obtained from solution in good yields, 80% and 62%, respectively. The measured PXRD patterns of all

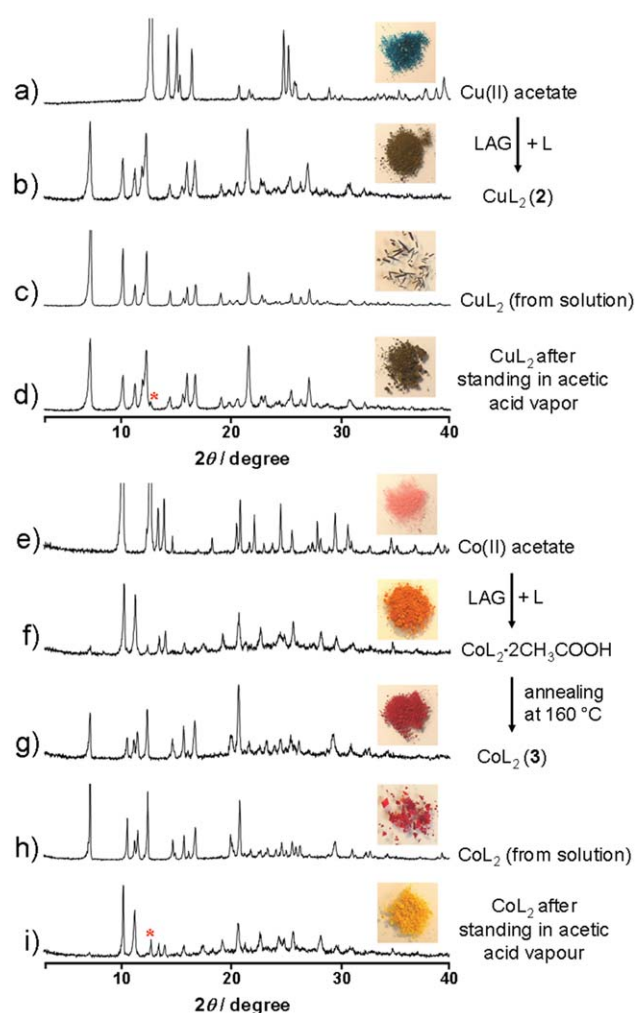


Fig. 1 PXRD patterns of: (a) copper(II) acetate monohydrate, (b) product after 60 min grinding of copper(II) acetate and compound **1**, (c) compound **2** prepared from solution, (d) compound **2** after two days standing in acetic acid vapour [reflection of small quantity of copper(II) acetate is labelled “*"], (e) cobalt(II) acetate tetrahydrate, (f) product after 60 min grinding of cobalt(II) acetate and compound **1**, *i.e.* acetic acid solvate of **3**, (g) product after annealing of the sample (f), *i.e.* compound **3**, (h) compound **3** prepared from solution, (i) compound **3** after three days standing in acetic acid vapour [reflection of small quantity of cobalt(II) acetate is labelled “*"].

compounds are in good agreement with those calculated from single crystal data, thus confirming that all products were obtained as pure single phases. The sharp reflections in the patterns testified to the crystallinity of the LAG products. Also, the PXRD patterns of both complexes, were almost identical, revealing the isostructurality of these two compounds (Fig. 1).

Liquid-assisted grinding of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with **1** in a 1 : 2 stoichiometric ratio afforded a dark green powder material of PXRD pattern identical to that of crystals prepared by the solution method (Fig. 1). Liquid-assisted grinding of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with **1** in a 1 : 2 stoichiometric ratio afforded an orange powder, a mixture of products, where the acetic acid solvate of **3** was present as a major product and the final product (compound **3**) in traces. This is evidenced by TG and FT-IR spectroscopy (observed weight loss 14.2%, calculated 15.9%; two

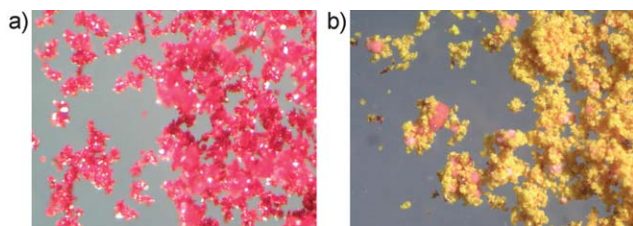


Fig. 2 Crystals of **3**: (a) before and (b) after three days standing in acetic acid vapour at room temperature.

molecules of acetic acid per formula unit). It was found that increasing the quantity of triethylamine in the reaction mixture leads to an increase in quantity of the final compound **3** in LAG product which can be observed by the darker orange colour of the product. Annealing of the sample (a mixture of products) at 160 °C for 60 min promoted the formation of a red powder. Its PXRD pattern matched with that of **3** prepared by the solution method (Fig. 1). The reverse reaction with acetic acid also proceeded in the solid state. When compound **3** was exposed to acetic acid vapour for three days at room temperature it reverts to a yellow powder, again a mixture of products but this time with acetic acid solvate as a major product and the metal acetate, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, in traces (Fig. 1 and 2). On the other hand, compound **2** has shown remarkably higher stability under the same conditions. Also, to explore the most appropriate LAG reaction conditions for both complexes we have carried out experiments with three different liquids: acetonitrile, methanol and triethylamine. Our LAG results indicated that all three liquids are suitable for Cu(II) complex synthesis, as revealed by PXRD, while for Co(II) complex synthesis the most suitable grinding liquid is the strongest base, triethylamine.¹²

In the FT-IR spectrum of **1** the strong band observed at 1618 cm^{-1} can be assigned to the C–N stretching vibration. The spectrum of **1** also shows several weak bands corresponding to aromatic C–H stretching (at 3057 cm^{-1} , 3029 cm^{-1} and 2918 cm^{-1}) and aromatic C–C stretching (1585 cm^{-1} and 1541 cm^{-1}). The absorption bands of the aromatic C–O and aromatic C–N stretching modes are centered at 1316 cm^{-1} and 1296 cm^{-1} , respectively. No strong band corresponding to N–H stretching was observed as a consequence of a strong intramolecular hydrogen bond, however, the weak and broad band centered at 3423 cm^{-1} was observed. The structural similarity of **2** and **3** is also observed from their FT-IR spectra. Their spectra are almost identical even in the fingerprint region. In the spectra of **2** and **3** the C–N stretching vibration band is shifted to a lower wave number, 1616 cm^{-1} and 1614 cm^{-1} , respectively. This decrease indicates the coordination of the amino group nitrogen to the metal ion, but it is relatively small in comparison with other similar complexes.¹³

Compound **1** crystallises in the monoclinic system with four molecules per unit cell. The keto-amino tautomer was detected from molecular geometry considerations where the C2–O1 and C11–N1 bond distances are in a good agreement with analogous values of corresponding Schiff bases derived from 2-hydroxy-1-naphthaldehyde. The shortened C3–C4 naphthalene ring bond distance of 1.341 Å suggests a quinoidal effect, caused probably by the typical and well known naphthalene tendency to keep its

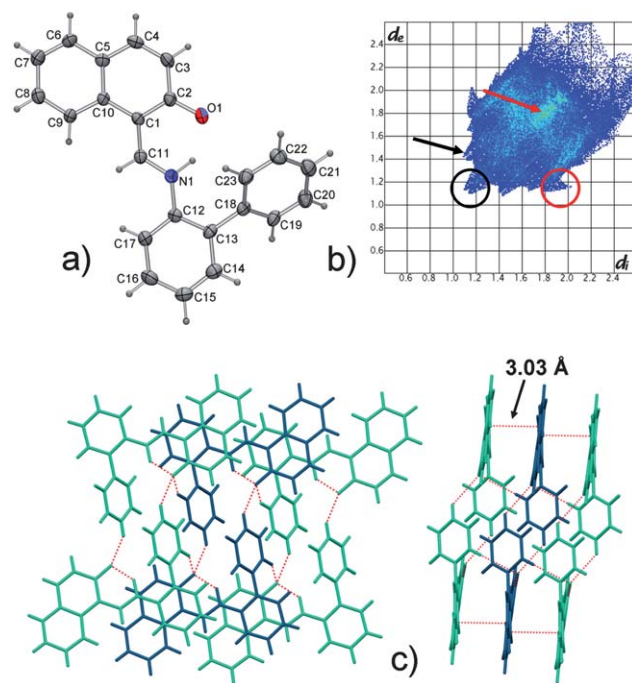


Fig. 3 Compound **1**: (a) view of the molecular structure, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius; (b) two-dimensional fingerprint plot (marked corresponding regions: red arrow for $\pi \cdots \pi$ contacts, black arrow for $\text{CH} \cdots \text{O}$ contacts, red circle for $\text{CH} \cdots \pi$ and black circle for short $\text{H} \cdots \text{H}$ contacts); (c) views of the packing, hydrogen bonding and π – π stacking.

D_{2h} bond lengths arrangement.^{14–16} The chelate ring including a strong intramolecular hydrogen bond with the bite distance N1–O1 2.547(2) Å is not completely coplanar with the naphthalene moiety where the corresponding dihedral angle is *ca* 6.1°. The molecule itself is not planar due to the twist of the phenyl ring connected on the amino nitrogen out of the naphthalene moiety plane with the corresponding dihedral angle *ca* 9.7°. The twisting of the biphenyl moiety is probably affected by the molecular environment and packing in the crystal. The discrete molecules of **1** are stacked in the [100] direction to give π -stacked 1D chains (Fig. 3). The distance between centroids defined by atoms C1/C2/C3/C4/C5/C10 and C12' [i: $x-1, y, z$] is *ca* 3.45 Å and the perpendicular distance between the planes defined by atoms of the naphthalene moiety is *ca* 3.03 Å (Fig. 2). The adjacent chains are further linked *via* weak intermolecular interactions (C21 \cdots O1ⁱⁱ separation 3.287(3) Å [ii: $1-x, 1-y, 1-z$] and C23 \cdots C23ⁱⁱⁱ separation 3.347(3) Å [iii: $1-x, -y, 1-z$]). Also, the described interactions can be observed by close analysis of the two-dimensional fingerprint plot derived from the Hirshfeld surface¹⁷ of the molecule of **1** (Fig. 3). In spite of the fact that the molar mass of **1** (323.4 g mol^{-1}) is relatively high, in comparison to the other similar Schiff bases, the lack of strong intermolecular interactions corresponds to a relatively low melting point.^{15,18} The DSC curve shows one endothermic peak at 132 °C (27.4 kJ mol^{-1}), which corresponds to the compound melting point. The TG curve presents no obvious weight loss from 25 to 170 °C. In the range between 170 and 490 °C, a mass loss of 99% can be attributed to evaporation and pyrolytic

decomposition. Nonisothermal melt-crystallisation DSC curves for **1** recorded at a cooling rate of $2\text{ }^{\circ}\text{C min}^{-1}$ show one exothermic peak at $97\text{ }^{\circ}\text{C}$, which corresponds to the melt crystallisation. It was found by PXRD that **1** crystallises from the melt into the same phase as from solution. There was no evidence of formation of another crystal form or amorphous phase, or of decomposition products.

The TG curves of **2** and **3** present no obvious weight loss from 25 to $290\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$, respectively. The curve of **2** exhibits two decomposition steps. The first step of the decomposition is smaller but in a wide temperature range which starts at $290\text{ }^{\circ}\text{C}$ and it is marked with the regular loss in mass up to $395\text{ }^{\circ}\text{C}$ (observed weight loss 36.5%). The second step of the decomposition continues on the first and is complete at $515\text{ }^{\circ}\text{C}$ (observed weight loss 52.2%). The observed residue at $600\text{ }^{\circ}\text{C}$ corresponds to CuO (observed 11.0% , calculated 11.2%). The TG curve of **3** exhibits one and relatively long decomposition step which starts at $290\text{ }^{\circ}\text{C}$ and completes at $515\text{ }^{\circ}\text{C}$ with a mass loss of 88.0% . The observed residue at $600\text{ }^{\circ}\text{C}$ corresponds to Co_3O_4 (observed 11.9% , calculated 11.4%). The measured PXRD patterns of residues for both compounds are in good agreement with calculated patterns.

The isostructural compounds **2** and **3** crystallise in the monoclinic system with four molecules per unit cell. The O and N donor atoms of bidentate ligands are positioned *cis* to each other. The form of the copper atom coordination polyhedron in **2** is irregular square planar, an intermediate conformation between square planar and tetrahedral with corresponding geometrical parameters: Cu1–N1 $1.964(2)\text{ \AA}$, Cu1–O1 $1.902(1)\text{ \AA}$, O1–Cu1–N1 $91.85(5)^{\circ}$ and *ca* 36.6° between O–Cu–N planes (Fig. 4). The form of the cobalt atom coordination polyhedron in **3** is irregular

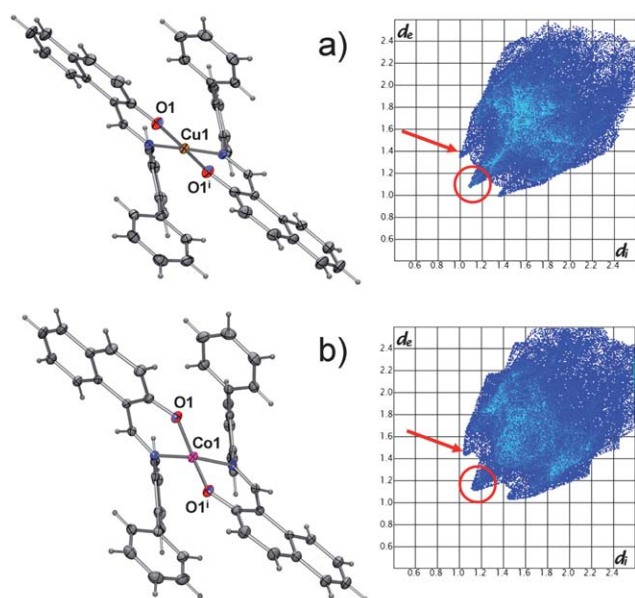


Fig. 4 A view of the molecular structures of **2** (a) and **3** (b) with corresponding two-dimensional fingerprint plots (the red arrow points to a region corresponding to C–H \cdots O contacts and the red circle indicates a region corresponding to short H \cdots H contacts). Displacement ellipsoids are drawn at the 30% probability level, H atoms are shown as small spheres of arbitrary radius. Atoms labelled with the letter “i” are at the symmetry position $1-x, y, 3/2-z$.

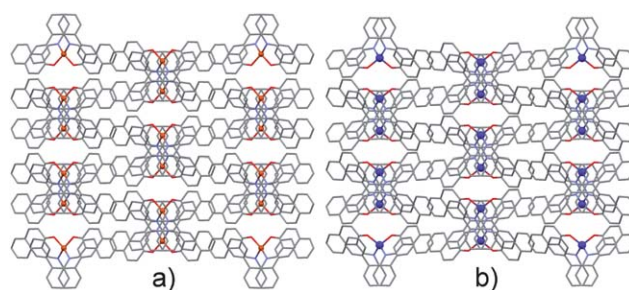


Fig. 5 Packing diagrams for compounds **2** (a) and **3** (b), viewed along the *c* axes. The metal atoms are shown as ball-and-stick models and C-bound H atoms have been omitted.

tetrahedron with corresponding geometrical parameters: Co1–N1 $1.989(2)\text{ \AA}$, Co1–O1 $1.905(2)\text{ \AA}$, O1–Co1–N1 $92.95(6)^{\circ}$ and *ca* 64.8° between O–Co–N planes (Fig. 4). As a result of proton substitution by the metal atom, the N1 \cdots O1 bite distance of **2** and **3** enlarges significantly to $2.777(2)\text{ \AA}$ and $2.825(2)\text{ \AA}$, respectively, compared to that in the free ligand. A close analysis of the two-dimensional fingerprint plots derived from the Hirshfeld surfaces¹⁷ of the molecules of both complexes, revealed weak hydrogen bonds (Fig. 4). An analysis of the crystal packing of **2** indicated C–H \cdots O and three C–H \cdots C interactions between neighbouring molecules. The C16 \cdots O1ⁱ and C15 \cdots C22^{iv} contacts, $3.373(2)$ and $3.709(2)\text{ \AA}$, respectively [*iv*: $x, y-1, z$] leads to the formation of chains which run parallel to the [010] direction. The chains thus formed interact by C–H \cdots C contacts between naphthalene rings of neighbouring molecules (C4 \cdots C8^v separation $3.336(2)\text{ \AA}$ [*v*: $3/2-x, y+1/2, 3/2-z$]), and also between biphenyl rings of neighbouring molecules (C23 \cdots C17ⁱⁱ separation $3.477(2)\text{ \AA}$ [*ii*: $1-x, 1-y, 1-z$]). Molecules of **3** are packed in the crystal in the same way as the molecules of **2** (Fig. 5), with small differences of intermolecular contacts. The C16 \cdots O1^{iv} and C15 \cdots C22^{iv} contacts, $3.484(3)$ and $3.733(4)\text{ \AA}$, respectively [*iv*: $x, y-1, z$] lead to the formation of chains which run parallel to the [010] direction. The chains thus formed interact by C–H \cdots C contacts between naphthalene and biphenyl rings of neighbouring molecules (C14 \cdots C9ⁱⁱ separation 3.639 \AA [*ii*: $1-x, 1-y, 1-z$]) and naphthalene rings of neighbouring molecules (C4 \cdots C8^v separation $3.415(3)\text{ \AA}$ [*v*: $3/2-x, y+1/2, 3/2-z$]). On further comparison of these two structures we notice that the shorter intermolecular contacts of **2** (density of 1.393 g cm^{-3}) lead to closer packing than that of the packing in **3** (density of 1.331 g cm^{-3}) which is also in correlation with the higher thermal stability of **2**.

Experimental

Preparations

All chemicals and solvents used in this work were commercially available and used without further purification. For preparation of **1**, 2-aminobiphenyl (1.69 g , 0.010 mol) and 2-hydroxy-1-naphthaldehyde (1.72 g , 0.010 mol) were dissolved at room temperature in methanol (15 mL and 30 mL , respectively). The solutions were mixed and the resulting mixture left at room temperature. Orange crystals appeared after a period of 1 day (Scheme 1).

Compound **2** was synthesised by liquid-assisted grinding together of 0.165 g of **1** (0.510 mmol) and 0.051 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.255 mmol) in the presence of 30 μL triethylamine. The compound **3** was synthesised by liquid-assisted grinding together of 0.154 g of **1** (0.476 mmol) and 0.059 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.237 mmol) in the presence of 40 μL triethylamine. Grinding was performed in a stainless steel jar of 10 mL volume, using two grinding balls of stainless steel, 7 mm in diameter. A Retsch MM200 grinder mill operating at 25 Hz frequency was used for the synthesis. Analysis of the product using PXRD revealed complete conversion of reactants into the products after 50 min grinding. The complex **2** was quantitatively obtained as a green powder and after annealing at 160 °C the complex **3** was quantitatively obtained as a red powder.

For solution-based synthesis of **2**, a clear solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.102 g, 0.51 mmol) in 30 mL methanol was added to a solution of **1** (0.330 g, 1.02 mmol) in 30 mL acetonitrile. The resultant mixture was refluxed for 2 h and the brown green precipitate was separated from the mother liquor by filtration, and washed with methanol. The compound **3** was synthesised analogously, the clear solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.130 g, 0.52 mmol) in 35 mL methanol was added to the solution of **1** (0.340 g, 1.05 mmol) in 30 mL acetonitrile. The resultant mixture was refluxed for 4 h and the rose red precipitate was separated from the mother liquor by filtration, and washed with methanol.

Single crystals of **1** suitable for X-ray diffraction were obtained from a mixture of tetrahydrofuran and amyl-alcohol (1 : 1) solution after 2 days. Single crystals of **2** were obtained by the liquid phase diffusion procedure from dichloromethane solution of both reactants (Schiff base and copper acetate). Single crystals of **3** were obtained by slow evaporation from a mixture of methanol and dichloromethane (1 : 1) solution.

Thermal and spectroscopic analysis

Thermal analysis was carried out on a Mettler Toledo TGA/SDTA 851 and DSC823 modules in sealed aluminium pans (40 μL). The compound **1** was heated in flowing nitrogen (200 mL min^{-1}) at a rate of 10 °C min^{-1} . The compounds **2** and **3** were heated in flowing oxygen (200 mL min^{-1}) at a rate of 7 °C min^{-1} . The data collection and analysis was performed using the program package *STAR[®] Software 9.01*.¹⁹ The non-isothermal crystallisation experiment were carried out under a nitrogen atmosphere with a flow rate of 50 mL min^{-1} . The experiment started with heating of the sample from 25 °C at a heating rate of 50 °C min^{-1} to the fusion temperature of compound **1** (132 °C). To ensure complete melting, the sample was kept at the respective fusion temperature for a holding period of 4 min. After this period the sample was cooled at a cooling rate of 10 °C min^{-1} . Infrared spectra were recorded on an EQUINOX 55 FTIR spectrophotometer using a KBr pellet. The data collection and analysis was performed using the program package *OPUS 4.0*.²⁰

X-Ray structure analysis

The crystal and molecular structures of **1**, **2** and **3** were determined by single crystal X-ray diffraction. The crystal data and

Table 1 General and crystallographic data for **1–3**

	1	2	3
Formula	$\text{C}_{23}\text{H}_{17}\text{NO}$	$\text{CuC}_{46}\text{H}_{32}\text{N}_2\text{O}_2$	$\text{CoC}_{46}\text{H}_{32}\text{N}_2\text{O}_2$
M_r	323.4	708.28	703.67
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P 2_1/c$	$C 2/c$	$C 2/c$
$a/\text{\AA}$	6.1078(2)	25.3539(10)	25.3808(13)
$b/\text{\AA}$	9.0766(3)	9.1936(2)	8.8392(4)
$c/\text{\AA}$	30.1945(11)	15.1458(6)	16.2656(10)
α (°)	90	90	90
β (°)	92.094(3)	106.930(4)	105.756(6)
γ (°)	90	90	90
$V/\text{\AA}^3$	1672.81(10)	3377.4(2)	3512.0(3)
Z	4	4	4
$D_x/\text{g cm}^{-3}$	1.284	1.393	1.331
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.71073	0.71073	0.71073
T/K	293	293	293
μ/mm^{-1}	0.078	0.691	0.531
$\rho_{\text{max}}, \text{min}/\text{e \AA}^{-3}$	0.126; −0.158	0.374; −0.208	0.512; −0.266
$R[F^2 > 4\sigma(F^2)]$	0.053	0.028	0.041
$wR(F^2)$	0.099	0.079	0.098
S	0.949	1.158	0.908

summary of the structure refinement are listed in Table 1. The diffraction data were collected at 292 K for all compounds. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. The data sets were collected using the ω scan mode over the 2θ range up to 54°. Programs CrysAlis CCD and CrysAlis RED²¹ were employed for data collection, cell refinement, and data reduction. The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.²² The structural refinement was performed on F^2 using all data. The C-bound hydrogen atoms were placed in calculated positions and treated as riding on their parent atoms [$\text{C-H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. The N-bound hydrogen atom for **1** were located in the difference Fourier map and fixed in its as-found position. All calculations were performed using the WINGX crystallographic suite of programs.²³ The molecular structures of compounds are presented by ORTEP-3²⁴ and POV-RAY²⁵ and their molecular packing projections were prepared by Mercury.²⁶ The powder X-ray diffraction (PXRD) experiments of the samples 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 50° (2θ) with steps of 0.02°, and the measuring time was 1 s per step. The data collection and analysis was performed using the program package *Philips X'Pert*.²⁷

Conclusions

Liquid-assisted grinding of Cu(II) and Co(II) acetates with bidentate Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde afforded mononuclear complexes. The heating process which follows the LAG reaction was revealed as a rapid and effective method for transformation of the complex mixture of LAG products to a pure mononuclear coordination compound. Also, LAG experiments with different liquids revealed that the rate of complex formation can depend on the

choice of the liquid. The rates of Cu(II) complex formation with acetonitrile, methanol and triethylamine are the same, while the rates of Co(II) complex formation differs remarkable. It seems that the most suitable liquid for Co(II) complex synthesis is the strongest base, triethylamine. This probably must be due to the formation of different LAG products. Experiments with Cu(II) resulted in the final complex and an additional liquid being formed, acetic acid, while experiments with Co(II) resulted in a solvate of Co(II) complex where the acetic acid remained in the crystal. Isostructural Cu(II) and Co(II) complexes exhibited similar thermal and spectroscopic properties, but a different chemical stability was observed. In the presence of acetic acid vapor at room temperature the mononuclear Co(II) complex decomposed to acetic acid solvate and its respective acetate salt. The Cu(II) complex has been shown to have a higher stability under the same conditions.

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