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# Reaction of sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl) benzenesulfonate with ethylenediamine on Cu(II) and Ni(II) centres: efficient Cu(II) homogeneous catalysts for cyanosilylation of aldehydes

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Reaction of sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzenesulfonate with ethylenediamine on Cu(II) and Ni(II) centres lead to variety of metal complexes which effectively catalyse the cyanosilylation of aldehydes with trimethylsilyl cyanide.

# Abstract

By reacting copper(II) or nickel(II) salts with sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl) benzenesulfonate (NaHL) in EtOH/H<sub>2</sub>O solvent mixture and in the presence of ethylenediamine (en), [Cu(HL)<sub>2</sub>(en)<sub>2</sub>] (1) or {[Ni(en)<sub>3</sub>](HL)<sub>2</sub>}·C<sub>2</sub>H<sub>5</sub>OH·6H<sub>2</sub>O (2) were synthesized, respectively. In MeOH, the coordination polymer [Cu( $\mu$ -L<sup>1</sup>-1 $\kappa$ O,NN'N'':2 $\kappa$ O')]<sub>n</sub> (3) was obtained, where L<sup>1</sup> refers to a dianionic ligand species attained via Schiff-base condensation of NaHL with en on the Cu(II) metal centre, whereas no reaction was obtained in the case of Ni(II). All the compounds were characterised by IR spectroscopy, ESI-MS, elemental and single-crystal diffraction. The Cu(II) compounds 1 and 3 act as effective homogenous catalysts for the cyanosilylation reaction of a variety of aldehydes with trimethylsilyl cyanide affording the corresponding cyanohydrin trimethylsilyl ethers in high yields (up to 93 %) and at room temperature.

*Keywords:* Arylhydrazones of  $\beta$ -diketones; Cu<sup>II</sup> and Ni<sup>II</sup> complexes; cyanosilylation of aldehydes.

# 1. Introduction

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Arylhydrazones of  $\beta$ -diketones (AHBDs) are well known models for the study of *E/Z* isomerism as well as azo-hydrazone tautomerism.<sup>1,2</sup> The molecular structures of AHBDs are characterized by strong intramolecular N–H···O or O–H···N resonance-assisted hydrogen bonds (RAHB), involving a set of conjugated single and double bonds.<sup>2</sup> Because of RAHB, the proton donor and acceptor atoms acquire partial opposite charges and strengthening of H-bond occurs. The position of the proton designates the nature of the donor functionality, which determines the reactivity of the AHBD and has an influence on intermolecular forces stabilizing the crystal structure.<sup>3</sup> Thus, RAHB reduces the reactivity of the donor and acceptor sites of AHBD compounds. For example, the carbonyl group involved in RAHB is not converted into a Schiff base in the reaction of AHBD with amines, whereas the ammonium salt is isolated.<sup>4</sup> A metal centre (for instance, of Cu<sup>2+</sup> or Ni<sup>2+</sup>) can promote the activation of a carbonyl group of an AHBD in its reaction with amines, leading to a variety of complexes with different nuclearities and intramolecular non-covalent interactions.<sup>2</sup>

On the other hand, cyanosilylation of carbonyl compounds with trimethylsilyl cyanide (TMSCN) (Scheme 1) to form new C–C bonds and to protect alcohol functions is an important reaction as the O-protected cyanohydrins can be transformed into a variety of building blocks, such as  $\alpha$ -hydroxy acids,  $\alpha$ -hydroxy ketones,  $\alpha$ -amino acids,  $\beta$ -amino alcohols, vicinal diols, 1,2-diamines, etc.<sup>5</sup> The reaction can be catalysed by various Lewis acids and bases.<sup>5</sup> For example, AlCl<sub>3</sub>, LaCl<sub>3</sub>, KCN/18 crown-6, Bu<sub>4</sub>N<sup>+</sup>CN<sup>-</sup>, trimethylsilyl triflate, amines, arsines, phosphines, phosphazanes, organocatalysts, etc. have been employed for this purpose.<sup>5</sup> In particular, the cyanosilylation of aldehydes does not require a strong Lewis acidity and can be carried out under mild conditions by using metal complexes as catalysts.<sup>6</sup> However, there are only a few metal complex approaches to this transformation in homogenous catalytic systems.<sup>6</sup>





Hence, on the basis of the above considerations, we focused this work on the following aims: i) to performe the reaction of an AHBD, *viz.* sodium 2-(2-(2,4-dioxopentan-3-ylidene) hydrazinyl)benzenesulfonate (NaHL), with ethylenediamine on Cu(II) and Ni(II) centres to prepare new stable complexes with strong Lewis acid metal sites; ii) to evaluate the catalytic activity of the prepared new complexes in the model cyanosilylation of aldehydes with trimethylsilyl cyanide (TMSCN), for which a high Lewis acid character of the catalyst should constitute a favorable feature (see below).

# 2. Results and Discussion

# 2.1. Synthesis of complexes 1-3

Sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzenesulfonate (NaHL) (Scheme 2) was synthesized by the Japp-Klingemann method<sup>7</sup> upon reaction between 2-sulfobenzenediazonium chloride and pentane-2,4-dione in water solution containing sodium hydroxide.

Reactions of copper(II) nitrate hydrate and nickel(II) acetate tetrahydrate with NaHL in the presence of ethylenediamine (en) in a mixture of EtOH/H<sub>2</sub>O (1:1, v/v) lead to the mononuclear compounds [Cu(HL- $\kappa$ O)<sub>2</sub>(en)<sub>2</sub>] (1) and {[Ni(en)<sub>3</sub>](HL)<sub>2</sub>}·C<sub>2</sub>H<sub>5</sub>OH·6H<sub>2</sub>O (2), respectively (routes I and II in Scheme 2). One-pot template reaction with copper(II) nitrate hydrate led to the coordination polymer [Cu( $\mu$ -L<sup>1</sup>-1 $\kappa$ O,NN'N'':2 $\kappa$ O')]<sub>n</sub> (3), where L<sup>1</sup> refers to the imino species derived from nucleophilic attack of en to a carbonyl group of NaHL (route III in Scheme 2). The formation of a novel Schiff base during complex formation is common.<sup>2</sup> We can tentatively explain the different behaviours of the Cu(II) and Ni(II) salts, as follows: copper(II) is expected to be a stronger Lewis acid than nickel(II) and thus it can activate more effectively the AHBD ligand towards a nucleophilic atack of the amine (en) to form the final L<sup>1</sup> ligand. Moreover, the acidity of the en ligand is promoted to a larger extent upon coordination to copper than to nickel, what favours the formation of water in the condensation reaction. Since Ni(II) is slightly softer than Cu(II) it is expected that the former prefers coordination to ligands containing softer donor atoms (en).

Compounds 1–3 were characterized by elemental analysis, IR spectroscopy, ESI-MS and single-crystal X-ray diffraction analysis. The IR spectra of both compounds show the v(NH), v(C=O) and  $v(C=O\cdots H)$  vibrations at 3245, 1675 and 1639 (for 1), and 3286, 1675 and 1642 cm<sup>-1</sup> (for 2) respectively, while for NaHL such bands are observed at 3114, 1679 and 1639 cm<sup>-1</sup>, correspondingly.<sup>7</sup> For such vibrations, polymer 3 displays values at 3364 and 3287 [v(NH)], 1674 [v(C=O)], and 1652 and 1608 [v(C=N)] cm<sup>-1</sup>. The ESI-MS peaks at 751.42 [Mr+H]<sup>+</sup> (for 1), 119.0 [Ni(en)<sub>3</sub>]<sup>2+</sup> and 283.0 [HL]<sup>-</sup> (for 2) and 388.8 [Mr+H]<sup>+</sup> (for 3) support the formulation of the compounds.



![](_page_4_Figure_3.jpeg)

# 2.2. Description of the X-ray crystal structures

Crystals of 1–3 suitable for X-ray diffraction analysis were obtained upon crystallization from EtOH/H<sub>2</sub>O (1:1, v/v) (for 1 and 2) or MeOH (for 3). The molecular structures are shown in Figure 1 and H-contacts in Figure S1. Crystallographic data and refinement parameters are given in Table S1 and selected bond distances and angles in Table S2.

The asymmetric unit of 1 includes a copper cation standing in an inversion centre and bound to an ethylenediamine molecule and a  $HL^{-}$  anion by one of the O-sulfonate atoms. Therefore, the complex molecule of 1 presents the metal in a slightly distorted octahedral geometry with four Natoms in the equatorial plan and two O-atoms in the apical sites. As a consequence of such a type of coordination, a RAHB remains, with a regular hydrogen bonding systems of HL<sup>-</sup>. The structure of **2** comprises two (hydrazinyl)benzenesulfonate anions that co-crystalized with a tris(ethylenediamine) nickel(II) cation. The anionic ligand in 1, as a whole, deviates from planarity as shown by the NCCC<sub>Me</sub> torsion angles of 11.6(3) and -167.9(2)°, and the angles of 20.06° and 20.34° between the least-square planes of the C<sub>Me</sub>CO groups, and that of the aromatic ring. Comparing with the structure of 2, those torsion angles assume values of 4.9(6) and -175.6(5) in one of the anions, and -3.7(6) and  $-174.8(4)^{\circ}$  in the other; the angles between the afore mentioned planes are as low as 14.68° and 11.49° in one anion and just 4.39° and 6.73° in the other, thus revealing the impact on coplanarity of coordination of HL<sup>-</sup> to a metal centre. However, such coordination had no effect either on the NN (see Table S1) or on the CketoneO bond distances and, in the latter case, the ketone groups of 1 and 2 not involved in the RAHB present slightly shorter lengths (by ca. 0.016 Å, Table S1) as comparated to the free ones. In addition, the HL<sup>-</sup> species in both compounds contains, besides the O<sub>ketone</sub>...N RAHB interactions [of 2.579(3) in 1, and 2.566(5) or 2.583(7) Å in 2; see Figures S1 and S2], also O<sub>sulfonvl</sub>...N charge assisted hydrogen bondings [CAHB; of 2.970(3) in 1,

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and 2.825(5) or 2.924(4) Å in **2**; see Figures S1 and S2], which relates to a synergistic mutual reinforcement of the intramolecular hydrogen bonding.

In the crystal structure of **3**, the copper atom has a square-pyramidal coordination sphere ( $\tau_5 = 0.05$ ) with the chelating ligand occupying the four equatorial positions and the apical site being engaged with an O-sulfonyl atom from an adjacent molecule, thus leading to a 1D coordination polymer that runs along the crystallographic *a* axis (Figure S1). Each metal cation is thus involved in two six-membered and one five-membered metallacycles *i.e.*, CuOSC<sub>2</sub>N, CuN<sub>2</sub>C<sub>2</sub>N and CuNC<sub>2</sub>N, respectively. The Cu–O<sub>equatorial</sub> distance of 1.9667(18) Å in **3** is considerably shorter than the Cu–O<sub>axial</sub> one, which assume the value of 2.528(2) Å, the latter being identical to that shown by **1** (Table S2). However, the Cu–N bond lenghts in **3** are in the range of 1.928(2) to 1.986(2) Å (Table S2) and are considerably shorter than those of **1** [*avg.* 2.012(2) Å]. This can conceivably be due to the extensive intermolecular hydrogen bond interactions in which compound **1** is involved and which expands the structure to a 3D network (Figure S4), while in **3** such interactions associate two infinite chains by means of the amine H-atoms that donate to the viccinal O-sulfonates (Figures S3 and S4). Despite of that, the intermolecular metal…metal distances are much shorter in **3** [5.407(1) Å] than in **1** [7.4179(4) Å, coincident with the *a* dimension of the unit cell].

![](_page_5_Figure_5.jpeg)

**Figure 1.** Molecular structures of 1-3 with partial atom numbering schemes. Symmetry codes to generate equivalent atoms: 1: *i*) -x,-y,-z; 3: *i*) 1+x,y,z: *ii*) -1+x,y,z. In 2 only one of the components of the disordered complex cation is shown.

# 2.3. Catalytic Activity

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The catalytic activity of the Cu(II) complexes 1 and 3 in the cyanosilylation reaction was tested under mild conditions and in air, with benzaldehyde as substrate. Several experimental variables were explored including catalyst amount, reaction temperature, reaction time, and type of solvent. These studies were carried out with complex 3 in view of its high solubility in the reaction medium (methanol) and are shown in Table 1.

Compounds 1 and 3 work as homogeneous catalysts, in methanol, for the conversion of benzaldehyde into 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (Scheme 1) at room temperature, with yields of 86 and 93 %, respectively, after 16 h (Table 1, entries 25 and 6). No other products were observed.

The plot of yield *versus* time for the cyanosilylation of benzaldehyde with catalysts **1** (Table 1, entries 20-25) and **3** (Table 1, entries 1-6) at 25 °C, is presented in Figure 2, showing an increase in the product yield with that factor. Extending the reaction time to 20 h did not increase the yield significantly.

Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	$T(^{\circ}\mathbb{C})$	Solvent	Yield <sup>b</sup> (%)	TON <sup>c</sup>
1	3	1	5	25	MeOH	22.5	4.5
2	3	2	5	25	MeOH	40.0	8.0
3	3	4	5	25	MeOH	46.5	9.3
4	3	6	5	25	MeOH	70.2	14.1
5	3	8	5	25	MeOH	77.6	15.5
6	3	16	5	25	MeOH	92.6	18.5
7	3	2	1	25	MeOH	23.7	24.0
8	3	2	3	25	MeOH	30.0	10.0
9	3	16	5	25	$CH_2Cl_2$	35.9	7.2
10	3	16	5	25	THF	45.4	9.1
11	3	16	5	25	CH <sub>3</sub> CN	29.6	5.9
12	3	10 min	5	50	MeOH	49.5	9.9
13	3	0.5	5	50	MeOH	61.7	12.3
14	3	1	5	50	MeOH	63.8	12.8
15	3	2	5	50	MeOH	72.9	14.6
16	3	4	5	50	MeOH	79.3	15.8
17	3	6	5	50	MeOH	82.7	16.5

Table 1. Cyanosilylation of benzaldehyde using 1 and 3 as catalysts.<sup>a</sup>

18	3	8	5	50	MeOH	84.8	17.0
19	3	16	5	50	MeOH	93.4	18.7
20	1	1	5	25	MeOH	46.2	9.3
21	1	2	5	25	MeOH	51.2	10.3
22	1	4	5	25	MeOH	55.6	11.1
23	1	6	5	25	MeOH	73.5	14.7
24	1	8	5	25	MeOH	82.0	16.4
25	1	16	5	25	MeOH	85.5	17.1
26	1	16	5	25	-	29.3	5.9
27	3	16	5	25	-	34.2	6.9
28	-	16	-	25	MeOH	22.1	-
29	-	16	-	25	-	13.0	-
30	Cu(NO <sub>3</sub> ) <sub>2</sub> · 2.5H <sub>2</sub> O	16	5	25	МеОН	28.9	5.8
31	2	16	5	25	МеОН	22.5	4.5

<sup>a</sup> Reaction conditions: solvent (2 mL), TMSCN (0.6 mmol) and aldehyde (0.4 mmol), in air. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of crude products (see Experimental part, Figure S5). <sup>c</sup> Number of moles of the product 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile, per mole of catalyst.

![](_page_7_Figure_5.jpeg)

Figure 2. Plots of yield vs. time for the cyanosilylation at 25 °C of benzaldehyde with TMSCN using catalysts 1 and 3, in methanol.

The set of experiments with different catalyst **3** loadings keeping the reaction time and temperature constant (Table 1, entries 2, 7 and 8) indicate that an increase of the catalyst amount from 1 to 5 mol% enhances the total yield from 24 up to *ca*. 40% (Figure 3-left), but leads to a significant decrease of the turnover number TON (moles of product per mole of catalyst) (Figure 3-right).

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![](_page_8_Figure_2.jpeg)

**Figure 3.** Effect of the catalyst **3** amount on the yield (left) and TON (right) for benzaldehyde cyanosilylation using TMSCN, in methanol.

Concerning the effect of time in the catalytic reaction, by keeping constant the solvent and the amount of catalyst **3** at a temperature of 25 °C (Table 1, entries 1–6) and 50 °C (Table 1, entries 12–19), one can observe that the conversion increases with the temperature (Figure 4). For example, a yield of 70% is obtained at 25 °C after 6 h (Table 1, entry 4), while a similar yield (73%) is reached at 50 °C after only 2 h (Table 1, entry 15). However, after 16 h the yield was the same for both temperatures (93%, Table 1, entries 6 and 19).

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![](_page_8_Figure_5.jpeg)

**Figure 4.** Plots of yield *vs.* time for benzaldehyde cyanosilylation with TMSCN using catalyst **3**, in methanol, at 25 °C and 50 °C (blue round and red square symbols, respectively).

The influence of the solvent, *viz.* methanol, dichloromethane, tetrahydrofuran (THF) or acetonitrile, in the catalytic reaction was also assessed, with polymer **3** as catalyst and under the aforementioned reaction conditions, resulting in yields of 93, 36, 45 and 30%, respectively (Table 1, entries 6 and 9–11). It is worthwhile to mention that **3** is not soluble in  $CH_2Cl_2$ , THF and in  $CH_3CN$ , and thus the catalytic reaction undergoes in a heterogeneous system. Despite the obvious advantage of the latter type of catalysis in what concerns the catalyst separation from the reaction medium, the results for the aldehyde conversion in methanol (homogeneous system) are much

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better, the reason why this was the chosen solvent. Moreover, under solvent free conditions, only 29 and 34% yields (with **1** and **3**, respectively; Table1, entries 26 and 27) were achieved, what may be a consequence of the heterogeneity of the system in such cases. A couple of blank reactions were also performed considering not only the absence of metal catalysts, but also the lack of both the catalyst and the solvent, giving yields of 22 and 13%, respectively (Table1, entries 28 and 29). In the presence of the Ni(II) complex **2**, the catalysis proceeded with only 22.5% yield (Table 1, entry 31).

The study of the influence of the type of aldehyde substrate was also performed, and various *para*-substituted aromatic aldehydes, as well as aliphatic ones, were used in the catalytic reaction. In all the cases, the corresponding cyanohydrin trimethylsilyl product was obtained, with yields ranging from 44 to 97 % (Table 2). Aromatic aldehydes bearing electron-donating substituents (methoxy or methyl) exhibit relatively lower reactivities (Table 2, entries 1 and 2) as compared to those having electron-withdrawing groups (bromo, chloro or nitro) (Table 2, entries 4–6), conceivably resulting from an increase of the substrate electrophilicity in the latter case. A series of aliphatic aldehydes, *viz*. acetaldehyde, propionaldehyde and hexanal, were also investigated (Table 2, entries 7–9), the results clearly showing that the aldehyde conversion decreases with the increase of the size of the aliphatic fragment (98% for acetaldehyde relatively to 65% for hexanal).

Entry	Substrate	Yield, % <sup>b</sup>	TON <sup>c</sup>
1	4-Methoxybenzaldehyde	44.5	8.9
2	4-Methylbenzaldehyde	58.8	11.8
3	Benzaldehyde	92.6	18.5
4	4-Bromobenzaldehyde	96.2	19.2
5	4-Chlorobenzaldehyde	96.8	19.3
6	4-Nitrobenzaldehyde	97.4	19.5
7	Acetaldehyde	98.0	19.6
8	Propionaldehyde	89.3	17.9
9	Hexanal	65.4	13.1

**Table 2.** Cyanosilylation of various aldehydes using TMSCN with catalyst  $3^{a}$ 

<sup>a</sup> Reaction conditions: 5 mol% of catalyst **3**, MeOH (2 mL), TMSCN (0.6 mmol) and aldehyde (0.4 mmol). Reaction time: 16 h. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of crude products (see Experimental part, Figure S5 and S6). <sup>c</sup> Number of moles of product per mole of catalyst.

The reaction mechanism is expected to be similar to that reported for related catalytic systems.<sup>6,8</sup> The Lewis acid copper(II) centre of **3** may activate the carbonyl group of the aldehyde towards the nucleophilic addition of the C=N group, followed by migration of the silyl group to the oxygen and subsequent product liberation.

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In comparison to the heterogeneous catalysis, the homogeneous catalysis of aldehyde cyanosilylation with TMSCN is not usual and scant examples were found in the literature.<sup>5,6,9</sup> The yields observed in this work are comparable with those obtained with other homogeneous metal complex catalysts, as well as with the chiral oxazaborolidinium ion catalysed cyanosilylation reaction (Table S3).<sup>6a,9</sup> However, in those systems, a longer reaction time, higher or lower (even negative) temperatures are required, what can be considered as disadvantages in comparison with our system.

# **3.** Conclusions

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Depending on the reaction conditions and on the nature of metal ions, sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzenesulfonate reacts with ethylenediamine leading to simple coordination of this amine or to its template Schiff base condensation and coordination of the derived species.

The obtained copper(II) complexes, in particular the coordination polymer  $[Cu(\mu-L^1-1\kappa O,NN'N'':2\kappa O')]_n$  (3), act as homogeneous catalysts, in methanol, for the cyanosilylation of aldehydes with trimethylsilyl cyanide, achieving excellent yields at room temperature and in reasonable reaction times. Moreover, it was found that electron-withdrawing substituents on the aromatic aldehydes promote the reaction yield, while an opposite effect was observed with the increase of the size of the alkyl group in the aliphatic substrates.

Our protocol is the first example of the application of a Cu(II)-AHBD (arylhydrazone of  $\beta$ diketone) complex as a homogeneous catalyst for the cyanosilylation of aldehydes. AHBDs are handily prepared compounds with easily tunable properties which can be applied to regulate and optimise the catalytic behaviour of their metal complexes, a direction which desirus to be explored in further studies.

#### 4. Experimental

#### 4.1. Materials and methods

All the chemicals were obtained from commercial sources and used as received. Infrared spectra  $(4000-400 \text{ cm}^{-1})$  were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a Perkin Elmer 2400 CHN Elemental Analyzer. Electrospray mass spectra were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). Catalytic aldehyde

conversions were calculated by solution <sup>1</sup>H NMR spectroscopy using a Bruker Avance 400 MHz spectrometer.

# 4.2. Synthesis of Complexes

#### 4.2.1. Synthesis of 1

A round bottom flask fitted with a condenser and a magnetic stirrer was charged with 0.5 mmol of copper(II) nitrate hemi(pentahydrate), 1 mmol of NaHL and 1 mmol of en in a 30 mL mixture of EtOH/H<sub>2</sub>O (1:1, v/v). The obtained brown solution was stirred under reflux for 3 h and then left in open air at room temperature for slow evaporation; green crystals of 1 suitable for X-ray measurements were obtained.

1: Yield, 62 % (based on Cu). Calcd. for  $C_{26}H_{38}CuN_8O_{10}S_2$  (*Mr* = 750.30): C 41.62, H 5.11, N 14.93; found C 41.89, H 5.00, N 14.81. ESI-MS: *m/z*: 751.42 [*Mr*+H]<sup>+</sup>. IR (KBr): 3340 and 3245 (s, br) v(NH), 1675 and 1639 (s) v(C=O), 1610 (s) v(C=N) cm<sup>-1</sup>.

#### 4.2.2. Synthesis of 2

In a round bottom flask fitted with a condenser and a magnetic stirrer, 0.5 mmol of nickel(II) acetate tetrahydrate were dissolved in a 30 mL mixture of EtOH/H<sub>2</sub>O (1:1, v/v), then 1 mmol of NaHL and 1.5 mmol of en were added. The obtained red solution was stirred under reflux for 3 h and then left in open air at room temperature for slow evaporation; brown crystals of **2** suitable for X-ray measurements were obtained.

**2:** Yield, 86 % (based on Ni). Calcd. for  $C_{30}H_{64}N_{10}NiO_{17}S_2$  (*Mr* = 959.74): C 37.55, H 6.72, N 14.60; found C 37.60, H 6.70, N 14.87. ESI-MS: *m/z*: 119.0 [Ni(en)<sub>3</sub>]<sup>2+</sup> and 283.0 [HL]<sup>-</sup>. IR (KBr): 3335 and 3286 (s, br) v(NH), 1675 and 1642 (s) v(C=O), 1605 (s) v(C=N) cm<sup>-1</sup>.

#### 4.2.3. Synthesis of 3

In a round bottom flask fitted with a condenser and a magnetic stirrer, 0.5 mmol of NaHL were dissoved in 20 mL of MeOH. To this stirred solution at ambient temperature were added 0.5 mmol of copper(II) nitrate hemi(pentahydrate) and 0.5 mmol of en. The reaction mixture was stirred under solvent reflux for 3 h and left at room temperature for slow evaporation; brown crystals of **3** suitable for X-ray measurements were obtained.

**3:** Yield, 36 % (based on Cu). Calcd. for  $C_{13}H_{16}CuN_4O_4S$  (*Mr* = 387.90): C 40.25, H 4.16, N 14.44; found C 40.47, H 3.83, N 14.91. ESI-MS: *m/z*: 388.8 [*Mr*+H]<sup>+</sup>. IR (KBr): 3364 and 3287 (s, br) v(NH), 1674 (s) v(C=O), 1652 and 1608 (s) v(C=N) cm<sup>-1</sup>.

#### 4.3. X-ray structure determinations

X-ray quality single crystals of the compounds were mounted in a nylon loop and measured at 150 K (3) or at room temperature (1 and 2). Intensity data were collected using a Bruker AXS-KAPPA

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APEX II (for 3) or a Bruker APEX-II PHOTON 100 diffractometer (for 1 and 2) with graphite monochromated Mo-K $\alpha$  ( $\lambda$  0.71069) radiations. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART<sup>10a</sup> software and refined using Bruker SAINT<sup>10b</sup> on all the observed reflections. Absorption corrections were applied using SADABS.<sup>10b</sup> Structures were solved by direct methods by using SIR-97<sup>10c</sup> and refined with SHELXL-2014.<sup>10d</sup> Calculations were performed using the WinGX System–Version 2014-1.<sup>10e</sup> The hydrogen atoms of hydrazine or amine groups were found in the difference Fourier map and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the belonging oxygen or nitrogen atoms, frequently with their distances restrained by using the DFIX command. Coordinates of hydrogen atoms bonded to carbon atoms were included in the refinement using the riding-model approximation with the Uiso(H) defined as 1.2Ueq of the parent aromatic or methylene atoms. The amine groups in 2 are disordered over two sites of occupancies 0.71:0.29 and were refined with the use of PART instructions. Probably because of such disorder, the amine H-atoms were not found but were inserted in calculated positions and the isotopic thermal parameters were set at 1.5 times the average thermal parameters of the belonging nitrogen atoms. There were disordered molecules in the structure of 2. All the attempts made to model them were not successful and they were removed using the SQUEEZE routine from Platon.<sup>10f</sup> Considering the number of electrons suppressed (88), the corresponding volume (374 Å<sup>3</sup>) and the microanalytical data, the unit cel should contain 1 molecule of ethanol and 6 water molecules (86 electrons) which were included in the model for final refinement. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed.

#### 4.4. Catalytic activity studies

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In typical experiment, to a solution of **1** or **3** (1–5 mol%) in solvent (2 mL) at room temperature was added aldehyde (0.4 mmol) followed by TMSCN (0.6 mmol). The resulting solution was stirred at room temperature in normal air for the appropriate time. The reaction mixture was then concentrated under vacuum, diluted with 3 mL water and extracted with diethyl ether (3x10 mL). After removal of diethyl ether under vacuum, the extract was taken for analysis by <sup>1</sup>H-NMR spectroscopy in CDCl<sub>3</sub>, to calculate the aldehyde conversion (product yield, since no other products were formed, Figure S5 and S6). The accuracy of this procedure was verified by repeating a number of the <sup>1</sup>H NMR analyses in the presence of 1,2-dimethoxyethane as internal standard, added to the CDCl<sub>3</sub> solution, what gave product yields similar to those obtained by the above method.

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**Supporting Information Available:** Crystal data, experimental parameters and selected details of the refinement calculations, selected bond distances and angles, hydrogen bond interactions and packing diagrams for compounds 1–3, as well as calculation of yield for the catalytic reaction. This material is available free of charge via the Internet at <u>http://pubs.rsc.org/</u> or from the authors. CCDC 1456524-1456526 contain the supplementary crystallographic data for 1–3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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