



## Research paper

# Synthesis, characterization and X-ray crystal structures of nickel(II) and copper(II) complexes derived from salicylaldehyde cyanoacetylhydrazone. An unexpected ligand transformation

Magdi F. Iskander<sup>a,\*</sup>, Tarek E. Khalil<sup>a</sup>, Sabine Foro<sup>b</sup><sup>a</sup> Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt<sup>b</sup> Material Science Department, Darmstadt Technical Univ., Alarich – Weiss Str 4, 64287 Darmstadt, Germany

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## ABSTRACT

Ni(II) complexes [Ni(L-CN)(H<sub>2</sub>O)<sub>3</sub>] (**1**), [Ni(L-CN)]<sub>2</sub> (**2**) and [Ni(HL-CN)]<sub>2</sub>·H<sub>2</sub>O (**3**) derived from salicylaldehyde cyanoacetylhydrazone (H<sub>2</sub>L-CN) have been prepared and characterized. Mixed ligand Ni(II) complexes [Ni(L-CN)HIm] (**4**) and [Ni(L-CN)HPyr]·0.1/2H<sub>2</sub>O (**5**), obtained respectively from the reaction of **2** with imidazole (HIm) and pyrazole (HPyr), have been isolated and characterized. The binuclear mixed ligand Cu(II) complex [Cu(L-CN)Py]<sub>2</sub> (**7**) has been also prepared from the reaction of [Cu(L-CN)]<sub>2</sub> (**6**) with pyridine (Py). Both **6** and **7** exhibit antiferromagnetic interaction with  $-2J$  values 340 cm<sup>-1</sup> and 1.23 cm<sup>-1</sup> respectively. Reaction of **6** with imidazole and pyrazole in methanol or ethanol proceeded with the transformation of the lateral -CH<sub>2</sub>CN residue of the hydrazone ligand to -COOR (R = Me or Et) and eventually gave the mixed ligand Cu(II) complexes [Cu(L-COOMe)HIm] (**8**), [Cu(L-COOEt)HIm] (**9**), [Cu(L-COOMe)HPyr·H<sub>2</sub>O] (**10**) and [Cu(L-COOEt)HPyr] (**11**). The X-ray molecular and supramolecular structures of **4**, **5**, **7**, **9** and **10** have been reported and discussed.

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## 1. Introduction

Alkanoyl- and aroylhydrazones derived from orthohydroxy aldehydes and ketones constitute a class of diprotic planar ONO tridentate chelating ligands [1–14]. In their metal complexes, this class of hydrazones can act as neutral [6], monoanionic [1,5–7,10–14] or dianionic [1–11] ONO tridentate ligands depending on the degree of deprotonation. To achieve the stable coordination number four or five (as in case of Ni(II) or Cu(II)) the central metal ion either coordinates to one or two neutral or mononegative monodentate ligand(s) [1,5–7,10,11,14] or dimerize through phenoxy oxygen bridges forming neutral [1–11] or dicationic [6–8,10–14] diphenoxy bridged centrosymmetric dimers. These types of dimers as well as other neutral and cationic mononuclear complexes have been used as a starting materials for the synthesis of metal(II) mixed ligand complexes [15–21]. The reaction of dinuclear metal (II) complexes with heterocyclic Lewis bases, (such as pyridine (Py), Imidazole (HIm), or pyrazole (HPyr)) afford either mononuclear, through the rupture of the diphenoxy bridges [15–17,19], or dinuclear mixed ligand complexes [18–21]. Dinuclear imidazolate or pyrazolate complexes have been also reported [16,17].

Different from salicylaldehyde acetylhydrazone, the analogous salicylaldehyde cyanoacetylhydrazone, hereafter abbreviated as H<sub>2</sub>L-CN (**1**), possess a reactive (-CH<sub>2</sub>CN) terminal side chain which can undergo acid or base catalyzed hydrolysis as well as metal mediated and metal catalyzed hydrolysis reactions [22]. Oxidative hydrolysis of -CH<sub>2</sub>CN using external oxidizing agent was also reported [23]. Mostafa et al. [24–26] claimed that reaction of H<sub>2</sub>L-CN with metal(II) chlorides, nitrates or sulphates in ethanol, isopropanol, or tert-butanol (as solvents) proceeded with the addition of one solvent molecule on the terminal cyano group, giving rise to the corresponding imidate complexes [24–26]. However, the reaction with metal(II) acetates gave the acetate complexes, [M(HL-CN)OAc·Sol] (M = Co, Ni or Cu and sol = H<sub>2</sub>O, EtOH or isopropanol) where the cyanoacetylhydrazone acts as monoanionic ONO tridentate ligand [24,25]. Different from these findings, the reaction of Co(II), Ni(II) or Cu(II) chloride or nitrate with H<sub>2</sub>L-CN in ethanol was reported to give varieties of cyanoacetylhydrazone metal(II) complexes with no singe of solvent addition on the cyano group [7,27]. The presence of the reactive lateral -CH<sub>2</sub>CN side chain in salicylaldehyde cyanoacetylhydrazone (**1**) and in continuation to our studies on mixed ligand Ni(II) and Cu(II) complexes derived from dianionic ONO [16,17,19,28], NNO [29] and NNS [30,31] tridentate ligands containing imidazole (HIm) and pyrazole (HPyr) as coligands, prompt interest to study the reaction of dinuclear

\* Corresponding author.

E-mail address: [m.iskander@link.net](mailto:m.iskander@link.net) (M.F. Iskander).

[[Ni(L-CN)]<sub>2</sub>] and [[Cu(L-CN)]<sub>2</sub>] complexes with imidazole and pyrazole in methanol and/or ethanol. For sake of comparison the reaction of [[Cu(L-CN)]<sub>2</sub>] with pyridine has been also studied. The structural characterization of the isolated new mixed ligand Ni(II) and Cu(II) complexes have been carried out aiming to explore any possible transformation of the coordinated ligand in these complexes.

## 2. Experimental

### 2.1. Materials used

Salicylaldehyde (prolabo), hydrazine hydrate (B.D.H) (99%), ethylcyanoacetate (Aldrich) and metal (II) salts (Fluka) were used as received without further purification. Cyanoacetic acid hydrazide was prepared from the reaction of ethylcyanoacetate with hydrazine hydrate as described previously [7]. N-salicylidene cyanoacetylhydrazine (H<sub>2</sub>L-CN) was prepared by the condensation of cyanoacetic acid hydrazide with salicylaldehyde as previously described [7]. All solvents were dried using standard methods.

### 2.2. Preparation of nickel(II) complexes

#### 2.2.1. Preparation of [Ni(L-CN)(H<sub>2</sub>O)<sub>3</sub>] (1)

A solution of H<sub>2</sub>L-CN (2.0 mmol., 0.41 g) in methanol (30 ml) was added drop wise, with constant stirring, to a solution of nickel acetate tetrahydrate (3.0 mmol, 0.75 g) in methanol (50 ml). The resulting mixture was stirred for 1 h, at room temperature, during which a yellowish green precipitate was formed. The precipitate, [Ni(L-CN)(H<sub>2</sub>O)<sub>3</sub>], was filtered, washed with methanol and then dried over silica gel. Yield: 58.0%. Anal. Calc. for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>Ni (%): C, 38.26; H, 4.17; N, 13.39 Found: C, 38.52; H, 3.92; N, 13.45. IR (KBr) (cm<sup>-1</sup>): 3400b ν<sub>asy</sub>(H<sub>2</sub>O); 3370 sh ν<sub>sy</sub>(H<sub>2</sub>O); 2940 s ν<sub>asy</sub>(CH<sub>2</sub>); 2900 s ν<sub>sy</sub>(CH<sub>2</sub>); 2265 m ν(C≡N); 1625 s ν(C=N=N=C). UV-vis (DMSO), λ<sub>max</sub>/nm (log ε): 304 (3.95); 316 (3.95); 360sh; 380sh; 390 (3.97). (+)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA%): 260.0 (260.8821) (100%) [Ni(L-CN) + H]<sup>+</sup>; 278.0 (278.8974) (72%) [Ni(L-CN) + H<sub>2</sub>O + H]<sup>+</sup>; 297.0 (296.9125) (51%) [Ni(L-CN) + 2H<sub>2</sub>O + H]<sup>+</sup>; 315.0 (314.9277) (10) [(Ni(L-CN) + 3H<sub>2</sub>O + H)<sup>+</sup>]; 325.0 (324.9662) (80%) [Ni(L-CN) + 2CH<sub>3</sub>OH + H]<sup>+</sup>; 520.0 (520.756) (24) [[Ni(L-CN)]<sub>2</sub> + H]<sup>+</sup>; 780.0 (780.6306) (14) [[Ni(L-CN)]<sub>3</sub> + H]<sup>+</sup>. (-)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA %): 259.0 (258.8663) (10) [[Ni(L-CN)]<sub>2</sub> - 2H]<sup>-</sup>; 291.0 (290.9084) (28) [[Ni(L-CN)]<sub>2</sub> + 2OCH<sub>3</sub>]<sup>-</sup>; 323.0 (322.9503) (35) [Ni(L-CN) + CH<sub>3</sub>OH + OCH<sub>3</sub>]<sup>-</sup>; 518.0 (518.7406) (100) [[Ni(L-CN)]<sub>2</sub> - H]<sup>-</sup>.

#### 2.2.2. Preparation of [[Ni(L-CN)]<sub>2</sub>] (2)

A solution of (H<sub>2</sub>L-CN) (2.0 mmol, 0.41 g) in absolute ethanol (30 ml) was added drop wise, with constant stirring, to a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.0 mmol, 0.50 g) in absolute ethanol (30 ml). Dry benzene (10 ml) was then added and the resulting mixture was boiled under reflux for 20 min. The formed [[Ni(L-CN)]<sub>2</sub>] was isolated by filtration, washed with dry diethyl ether, then dried under vacuum. Yield: 72.0%. Anal. Calc. for C<sub>20</sub>H<sub>14</sub>N<sub>6</sub>O<sub>4</sub>Ni (%): C, 46.22; H, 2.71; N, 16.17 Found: C, 46.12; H, 2.92; N, 15.87. IR (KBr) (cm<sup>-1</sup>): 2940 s ν<sub>asy</sub>(CH<sub>2</sub>); 2900 s ν<sub>sy</sub>(CH<sub>2</sub>); 2265 m ν(C≡N); 1625 s ν(C=N=N=C). UV-vis (DMSO), λ<sub>max</sub>/nm (log ε): 305 (4.02), 316 (3.93), 360sh, 380sh, 390 (3.95). (+)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA%): 260.4 (260.8821) (62) [[Ni(L-CN)]<sub>2</sub> + 2H]<sup>+</sup>; 325.0 (324.9662) (28) [Ni(L-CN) + 2CH<sub>3</sub>OH + H]<sup>+</sup>; 521.0 (520.7564) (100) [[Ni(L-CN)]<sub>2</sub> + H]<sup>+</sup>. (-)ESI MS (DMF/Methanol, 1:10 v/v) z/m (calc) (RA%): 259.0 (258.8663) (42) [[Ni(L-CN)]<sub>2</sub> - 2H]<sup>-</sup>; 291.0 (290.9084) (100) [[Ni(L-CN)]<sub>2</sub> + 2CH<sub>3</sub>O]<sup>-</sup>; 322.0 (322.9503) (63) [Ni(L-CN) + CH<sub>3</sub>OH + CH<sub>3</sub>O]<sup>-</sup>;

(518.7406) (72) [[Ni(L-CN)]<sub>2</sub> - H]<sup>-</sup>; 582.0 (582.8246) (30) [[Ni(L-CN)]<sub>2</sub> + CH<sub>3</sub>OH + CH<sub>3</sub>O]<sup>-</sup>.

#### 2.2.3. Preparation of [Ni(HL-CN)]<sub>2</sub>·H<sub>2</sub>O (3)

A solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.0 mmol, 0.50 g) in methanol (25 ml) was added drop wise to a boiling solution of H<sub>2</sub>L-CN (5.0 mmol, 1.02 g) in methanol (25 ml). The reaction mixture was boiled under reflux for 1 h. then left to cool at room temperature. The green [Ni(HL-CN)]<sub>2</sub>·H<sub>2</sub>O which was formed, was filtered out, washed with dry diethyl ether then dried in air. Yield: 66%. Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>6</sub>O<sub>5</sub>Ni (%): C, 49.93; H, 3.77; N, 17.47. Found: C, 50.12; H, 3.61; N, 17.48%. IR (KBr) (cm<sup>-1</sup>): 3425 b ν<sub>asy</sub>(H<sub>2</sub>O); 3200 s ν(N-H); 2952 m ν<sub>asy</sub>(CH<sub>3</sub>); 2929 m ν<sub>asy</sub>(CH<sub>2</sub>); 2265 m ν(C≡N); 1635 s amide I [ν(C=O)], 1590 ν(C=C), 1565 s ν(C=N); 1525 m amide II [δ(N-H) + ν(C-N)]. UV-vis (DMSO), λ<sub>max</sub>/nm (log ε): 300 (3.98); 325 (3.73); 385 (3.65); 620 (1.82); 1000 (0.85). (+)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA%): 260.0 (260.882) (100) [[Ni(L-CN)]<sub>2</sub> + 2H]<sup>+</sup>; 278.2 (278.897) (75) [Ni(HL-CN) + H<sub>2</sub>O]<sup>+</sup>; 462.0 (462.0663) (20) [Ni(L-CN)<sub>2</sub> + H]<sup>+</sup>; 520.0 (520.756) (28) [[Ni(L-CN)]<sub>2</sub> + H]<sup>+</sup>; 779.7 (780.6306) (22) [[Ni(L-CN)]<sub>3</sub> + H]<sup>+</sup>. (-)ESI MS (DMF/Methanol 1: 10 v/v) z/m (calc) (RA%): 259.0 (258.8663) (37) [Ni(L-CN) - H]<sup>-</sup>; 284.0 (283.8949) (36) [[Ni(L-CN)]<sub>2</sub> + OH + OCH<sub>3</sub>]<sup>-</sup>; 393.0 (392.5082) (45) [[Ni<sub>2</sub>(HL)<sub>3</sub> + 2OCH<sub>3</sub> - H]<sup>-</sup>; 462.0 (262.0663) (100) [Ni(HL)<sub>2</sub> - H]<sup>-</sup>; 721.0 (721.9404) (35) [[Ni<sub>2</sub>(HL)<sub>3</sub> - 2H]<sup>-</sup>.

#### 2.2.4. Preparation of [Ni(L-CN)HIm] (4)

To a suspension of [Ni(L-CN)·3H<sub>2</sub>O] (2.0 mmol, 0.63 g) in dry methanol (30 ml), a solution of imidazole (5.0 mmol., 0.39 g) in dry methanol (30 ml) was added drop wise with constant stirring. The resulted reaction mixture was boiled under reflux for 1 h. then evaporated to half of its volume. On cooling the red crystalline product, [Ni(L-CN)HIm], was separated out by filtration, washed with diethylether then dried in *vacuo*. Yield: 65%. Anal. Calc. for C<sub>13</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>Ni (%): C, 47.61; H, 3.38; N, 21.35, Found: C, 47.45; H, 3.32; N, 21.42. IR (KBr) (cm<sup>-1</sup>): 3158 s ν(N-H) imidazole; 2955 m ν<sub>asy</sub>(CH<sub>2</sub>), 2854 m ν<sub>sy</sub>(CH<sub>2</sub>), 2256 m ν(C≡N), 1620 s ν(C=N=N=C). UV-vis (methanol), λ<sub>max</sub>/nm (log ε): 288 (3.10), 308 (3.84), 350 (3.99), 382 sh, 398 sh. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS, ppm): 13.26 (1H, imidazole NH); 7.68 (1H, imidazole CH); 7.10 (2H, imidazole CH); 8.13 (1H, C=N-CH); 7.42 (1H, aromatic); 7.18 (1H, aromatic); 6.85 (2H, aromatic); 3.65 (2H, CH<sub>2</sub>CN). (+)ESI MS (Methanol) z/m (calc) (RA%): 260.2 (260.882) (36) [[Ni(L-CN)]<sub>2</sub> + 2H]<sup>+</sup>; 328.2 (328.960) (100) [Ni(L-CN)HIm + H]<sup>+</sup>; 520.1 (520.756) (19) [[Ni(L-CN)]<sub>2</sub> + H]<sup>+</sup>; 543.0 (542.738) (35) [[Ni(L-CN)]<sub>2</sub> + Na]<sup>+</sup>; 802.2 (802.613) (10) [[Ni(L-CN)]<sub>3</sub> + Na]<sup>+</sup>. (-)ESI MS (Methanol) z/m (calc) (RA%): 326.0 (326.944) (7) [Ni(L-CN)HIm - H]<sup>-</sup>; 584.9 (586.818) (100) [[Ni(L-CN)]<sub>2</sub>Im]<sup>-</sup>.

#### 2.2.5. Preparation of [Ni(L-CN)HPyr]0.1/2H<sub>2</sub>O (5)

This complex was prepared using the same procedure described for [Ni(L-CN)HIm] using pyrazole instead of imidazole. Yield: 63%. Anal. Calc. for C<sub>13</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>Ni.1/2 H<sub>2</sub>O (%): C, 46.34; H, 3.59; N, 20.78, Found: C, 46.46; H, 3.59; N, 20.56. IR (KBr) (cm<sup>-1</sup>): 3190 ν(N-H) pyrazole; 2954 ν<sub>asy</sub>(CH<sub>2</sub>); 2850 ν<sub>sy</sub>(CH<sub>2</sub>); 2255 ν(C≡N); 1615 ν(C=N=N=C). UV-vis (methanol), λ<sub>max</sub>/nm (log ε); 284 sh (4.03); 294 (4.10); 308 (4.05); 352 (3.96); 374 sh (3.93). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS, ppm): 13.50 (1H, pyrazole NH); 7.52 (2H, pyrazole CH); 6.30 (1H, pyrazole CH); 6.82 (2H, aromatic); 7.15 (1H, aromatic); 7.45 (1H, aromatic), 8.12 (1H, C=N-CH); 3.02 (2H, CH<sub>2</sub>CN). (+)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA%): 261.0 (260.882) (20) [[Ni(L-CN)]<sub>2</sub> + 2H]<sup>+</sup>; 278.0 (278.897) (58) [[Ni(L-CN)·H<sub>2</sub>O]<sub>2</sub> + 2H]<sup>+</sup>; 328.0 (328.960) (100) [Ni(L-CN)HPyr + H]<sup>+</sup>; 521.0 (520.756) (20) [[Ni(L-CN)]<sub>2</sub> + H]<sup>+</sup>; 540.9 (542.738) (82) [[Ni(L-CN)]<sub>2</sub> + Na]<sup>+</sup>; 802.0 (802.6125) (39) [[Ni(L-CN)]<sub>3</sub> + Na]<sup>+</sup>. (-)ESI MS (DMF/Methanol, 1: 10 v/v) z/m (calc) (RA%): 277.9 (276.882)

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