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Synthesis, crystal structure, antimicrobial activity and electrochemistry study of chromium(III) and copper(II) complexes based on semicarbazone Schiff base and azide ligands

B. Shaabani^{a,*}, A.A. Khandar^a, M. Dusek^b, M. Pojarova^b, F. Mahmoudi^a

^a Department of Inorganic Chemistry, Faculty of Chemistry, Tabriz University, Tabriz 51666-14766, Iran ^b Institute of Physics of the ASCR, v.v.i, Na Slovance 218221 Prague 8, Czech Republic

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ABSTRACT

A tridentate NNO donor Schiff base ligand $HL = [HL: C_5H_4NCH=NNHCONH_2]$ was obtained by condensation of pyridine 2-carbaldehyde with semicarbazide. The HL and azide ligands with Cr(III) and Cu(II) ions have been used to synthesize a dinuclear complex $[Cr(L)(N_3)(OCH_3)]_2$ (1) and a coordination polymer complex $[Cu(L)(N_3)]_n$ (2). The ligand, 1 and 2 were clearly characterised by elemental analysis, FT-IR, UV–Vis spectral studies and the structures of the 1 and 2, have been studied by single crystal X-ray diffraction analysis. The results of X-ray diffraction analysis revealed Cr(III) and Cu(II) center are coordinated in a distorted octahedral and a square pyramidal geometries for 1 and 2 respectively. The ligand and the complexes were tested for their efficiency towards antimicrobial activity and the MIC data revealed that the HL, 1 and 2 have not strong activity in comparison to the standard drugs. The electrochemistry of the HL and its complexes were studied by cyclic voltammetry.

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1. Introduction

In the recent years, the design and synthesis of metal-organic frameworks (MOFs) have attracted much attention from chemists. These compounds have potential applications in the field of molecular storage, separation, catalysis, and drug delivery [1-5]. The Schiff base ligands play an important role in inorganic chemistry as they are readily available and easily form stable complexes with most transition metal ions [6–8]. Schiff bases are also important intermediates in synthesis of some bioactive compounds [8-12] and are potent anti-bacterial, anti-fungal, anticancer and antiviral compounds [12-23]. Semi- and thiosemicarbazones belong to the family of Schiff bases and are known as Structural isomers E, E, Z [24-26]. Semicarbazones can coordinate to the metal either as neutral or deprotonated ligands through two or three hetero atoms [25–27] also these ligands have wide spectrum of biological applications [22-28]. The first report of the pyridine 2-carbaldehyde semicarbazone ligand is in the literature dated from 1955 [28-32] and described its pharmaceutical potential as an antifungal agent. Another kind of ligands are pseudohalides which can form the bridging complexes with transition metals where the groups N3⁻, NCS⁻, NCO⁻ coordinate in the end-to-end and end-on bridging modes [23-40].

More recently dinuclear copper(II) and cobalt(III) complexes with pyridine 2-carbaldehyde semicarbazone and azide ligands were crystallographically characterized [32]. We herein report on the synthesis, characterization and X-ray crystal structure analysis of two chromium(III) and copper(II) complexes with pyridine 2carbaldehyde semicarbazone and azide ligands. Also the electrochemistry study and antimicrobial activity of free ligand HL and the complexes **1** and **2** are discussed.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were of reagent grade and were used without purification except HL, which was prepared with reflux method according to the literature procedures [28-32]. Other reagents were purchased from Merck or Fluka and were used without further purification.

2.2. Synthesis of the Schiff base ligand (HL)

Schiff base ligand HL [HL: $C_5H_5NCH=NNHCONH_2$] was prepared by condensation of pyridine 2-carbaldehyde with semicarbazide with reflux method according to literature procedure [28–32].



^{*} Corresponding author. Tel.: +98 411 3393144; fax: +98 411 3340191. *E-mail address:* b.shaabani@yahoo.com (B. Shaabani).

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Caution! Metal azide complexes are potentially explosive. Only a small amount of material should be prepared and should be handled with caution.

2.3. Synthesis of $[Cr(L)(N_3)(OCH_3)]_2$ (1)

The crystals of complexes are obtained by slow diffusion in an H-shaped tube [41–43]. In this method of synthesis, the HL (0.04 g, 0.2 mmol) was placed into one arm of an H-tube, and Cr(NO₃)₃.9H₂O (0.08 g, 0.2 mmol) and NaN₃ (0.08 g,1.2 mmol) were placed into the other arm. Then 25 mL of methanol was carefully added until the bridge of the tube was filled. After 4 days slow diffusion between the two solutions, pure dark blue crystals (decomposed in 310 °C) formed, which were isolated, filtered off, washed with acetone and diethyl ether and dried in air. Yield: 0.015 g, 30%. *Anal.* Calc. for C1₆H₂₀Cr₂N₁₄O₄: C, 33.31; H, 3.47; N, 34.00. Found: C, 33.43; H, 3.47; N, 34.01%. Characteristic IR absorptions (cm⁻¹): 3411 m, v(NH₂); 1609 s, v(C=N); 1154 s, v(NN); 1645 s, v(C=O); 2060 s, v(N₃⁻).

2.4. Synthesis of $[Cu(L)(N3)]_n$ (2)

Using similar method as for **1**, the HL (0.04 g, 0.2 mmol) and Cu(OAC)₂.H₂O (0.04 g, 0.2 mmol) and NaN₃ (0.12 g, 1.8 mmol) in ethanol solvent were used. After 4 days, slow diffusion between the two solutions, pure dark green crystals (decomposed in 170 °C) formed, which were isolated, filtered off, washed with acetone and diethyl ether and dried in air. Yield: 0.08 g, 40%. *Anal. Calc.* for C7H7CuN7O: C, 31.25; H, 2.60; N, 36.46. Found: C, 31.37; H, 2.60; N, 36.56%. Characteristic IR absorbtions (cm⁻¹): 3433 m, v(NH2); 1606 s, v(C=N); 1164 s, v(NN); 1638 s, v(C=O); 2068 s, $v(N_3^{-})$.

2.5. Physical measurements

NMR spectra were recorded on Bruker Avance 400 in DMSO solvent with SiMe4 as internal standard at room temperature. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a FT-IR Spectrometer Bruker Tensor 27 in the region $4000-400 \text{ cm}^{-1}$ using KBr pellets. Electronic spectra were recorded on a Shimadzu, UV-1650 PC spectrophotometer from solution in DMSO at 300 K. Cyclic voltammetric measurements were performed using an AMEL Instruments Model 2053 as potentiostate connected with a function generator (AMEL Model 568). In all electrochemical studies, a three-electrode system was used consisting of a glassy carbon as the working electrode, a platinum wire auxillary electrode, and an Ag/AgCl as the reference electrode. All of the electrochemical experiments were carried out under nitrogen atmosphere at room temperature using solution of complexes with concentration about 10⁻³M in DMSO solvent containing 0.1 M lithium perchlorate as the supporting electrolyte. Electrochemistry of the ligand HL and its metal compounds and azide, were studied by cyclic voltammetry in scan rate of 0.010 V s⁻¹ in DMSO solution containing 0.1 M lithium perchlorate supporting electrolyte. Ferrocene (Fc) was used as the internal standard and all redox potentials were referenced to the Fc $^{+/0}$ couple.

2.6. Single-crystal X-ray diffraction

X-ray diffraction data was collected at 120 K with four-circle diffractometer Gemini of Oxford Diffraction, Ltd., using a sealed X-ray tube. The primary beam was collimated by mirrors using the Enhance-Ultra collimator; the diffracted beam was detected

with the CCD detector Atlas. Standard data collection strategy of CrysAlis [44] was used for data collection.

2.7. Antimicrobial activity

The free ligand and metal complexes were screened for their antimicrobial activities against the bacterias Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Erwinia carotovora and fungi Candida kefyr, Candida krusei, Aspergillus niger by the disc diffusion method as Gram negative, Gram positive and fungal organisms, respectively. The Muller hinton agar and Sabouraud dextrose agar were used to culture bacteria and fungi, respectively. The culture media was poured into sterile plates and microorganisms were introduced on the surface of agar plates individually. The blank sterile discs measuring 6.4 mm in diameter were soaked in a known concentration of the test compounds. Then the soaked discs were implanted on the surface of the plates. A blank disc was soaked in the solvent (DMSO) and implanted as negative control on each plate along with the standard drugs. The plates were incubated at 37 °C (24 h) and 27 °C (48 h) for bacterial and fungal strain, respectively. The MIC for each tested substance was determined by macroscopic observation of microbial growth. It corresponds to the well with the lowest concentration of the tested substance where microbial growth was clearly inhibited.

3. Results and discussion

3.1. Infrared spectra analyses

The IR spectra of **1** and **2** were analyzed and compared with that of the free ligand and are listed in Table 1. A medium band in the range at 3162 cm⁻¹ in the free ligand due to a $v(^{3}N-H)$ vibration, disappears in the spectra of complexes 1 and 2, providing strong evidence for ligand coordination to the metal ions in monoanionic form L⁻ by losing its hydrogen [27]. The strong band at 3345 cm⁻¹ in the spectra of HL, assigned to $v({}^{4}N-H)$, shift to higher energies and demonstrate at 3411 and 3433 cm⁻¹ in **1** and **2**. The strong v(C=N) bands of semicarbazone around 1613 cm⁻¹, are found to be shifted to lower frequencies in the complexes indicating coordination via the azomethine nitrogen [4,1,27]. The coordination of this nitrogen is also supported by a shift in v(N–N) to higher frequencies in the complexes (for more information see the Table 1). Observation of a very strong absorption band in 2000–2100 cm⁻¹ is related to the coordination of azide ligand to the metal centers in these complexes [27,33,39,45]. This band is observed at 2060 and 2068 cm^{-1} for **1** and **2**, respectively.

3.2. Electronic spectra

Electronic spectrum of the ligand shows an absorption maximum at 300 nm attributed to intra-ligand $\pi \rightarrow \pi^*$ transitions of the pyridyl ring and imine function of the semicarbazone moiety [27]. The shift of the $\pi \rightarrow \pi^*$ bands to the longer wavelength region is caused by the weakening of the C=O bond and enhancement of the conjugation system after the complex formation [27]. The bands related to these transitions are evident in the range 308 and 302 nm for **1** and **2**. The UV absorption bands exhibit a charge

Table 1 Infrared spectra (cm^{-1}) assignment for HL, 1 and 2.

Compound	$v_{\rm NH2}$	v _{NH}	$v_{C=0}$	$v_{C=N}$	V _{N-N}	v_{N3}
HL	3345	3162	1685	1613	1091	-
Complex 1	3411	-	1645	1609	1154	2060
Complex 2	3433	-	1638	1606	1164	2068

transfer transition in the range 360–410 nm for **1** and **2** probably assignable to the azide ligand to metal charge transfer transition [46–48]. For **1** containing distorted octahedral chromium(III) centers, a weak band at 500–700 nm appeared due to ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transition [47–49], while the higher energy band ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ was obscured by ligand to metal charge transfer bands obtained in the broad band 360–410 nm. The spectrum of **2** displays a broad band at 650 nm due to ${}^{2}E \rightarrow {}^{2}T_{2}$ transition and it is consistent with the square pyramidal geometry for copper(II) complexes [46].

3.3. Crystal structures

The complexes $[Cr(L)(N_3)(OCH_3)]_2$ (1) and $[Cu(L)(N_3)]_n$ (2) were isolated in a form suitable for single-crystal X-ray diffraction analysis.

3.3.1. Structure of [Cr(L)(N₃)(OCH₃)]₂ (1)

The structure of complex **1** is depicted in Fig. 1 and the crystal data and structure refinement of 1 are summarized in Table 2. Single X-ray crystal analysis revealed, dinuclear species of Cr(III) with two methoxy groups, which are acting as bridging groups and are linking two Cr(III) centers into dinuclear units. Also each Cr(III) center is coordinated to a azide ligand in terminal mode. The methoxy groups in 1, are obtained from the methanol which was used as solvent for synthesis of the complex. In 1, the Schiff base ligand is deprotonated and coordinated to Cr(III) center as a monoanionic ligand, which was also proven by the FT-IR spectral data. Both of Cr(III) centers are symmetry equivalent and their coordination can be best described as a distorted octahedral with CrO₃N₃ chromophore. The basal plane is formed by the pyridine and azometine nitrogen atoms (N1 and N2), the oxygen atom which constitutes the semicarbazone NNO chelating set (O1), and the oxygen atom from the methoxy group (O2). The azide nitrogen atom (N5) and the oxygen from another methoxy group (O2), form the apical vertices at longer distances [N5-Cr1, 2.001(4) Å and O2-Cr1, 1.972(3) Å]. The octahedral geometry around Cr(III) is strongly distorted. with [N5-Cr1-N1: 89.69(16)° and N5-Cr1-O2: 171.79(15)°]. The Cr1...Cr1 distance for the dinuclear unit is 3.052 Å (Detailed information about bond lengths and angles in the chromium coordination environment can be found in Table 3). The chelate bite angles in the two five-membered rings are close [O1-Cr1-N2; 76.91(14)° and N2-Cr1-N1; 78.92(15)°]. Azide ions



Fig. 1. Crystal structure representation of the binuclear complex $[Cr(L)(N_3)(OCH_3)]_2$ (1).

Table 2

Crystal and structure refinement data for complexes (1) and (2).

	Complex 1	Complex 2
Formula Formula weight Crystal description Crystal size (mm) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z ρ_{calc} (g cm ⁻³) μ (mm ⁻¹) θ range (°) Final <i>R</i> indices [$l > 2\alpha(l)$]	Complex 1 C ₁₆ H ₂₀ Cr ₂ N ₁₄ O ₄ 576.42 Dark blue plate 0.17 × 0.12 × 0.06 120 K monoclinc P21/n 8.7622(2) 11.1757(2) 11.1757(2) 11.8550(2) 90 105.214(2) 90 1121.14(4) 2 1.707 8.507 66.967 0.0625	Complex 2 $C_7H_7CuN_7O$ 268.74 Green plate 0.18 × 0.08 × 0.04 120 K monoclinc P21/c 10.52999(14) 11.13677(15) 8.09356(12) 90 99.07(14) 90 934.97(2) 4 1.90 3.26 67.030 0.0303
Final <i>R</i> indices (all data)	0.0896	0.0775
Final <i>R</i> indices (all data) Largest difference in peak and hole	0.0896 0.60; -0.59	0.0775 0.40; -0.45
(e A ⁻³)		

Table 3				
Selected bond	lengths (Å)	and angles	(\circ) for (1)	and (2)

89.69(16)

91.67(16)

N1-Cr1-N5

N2-Cr1-N5

1		2	
Cr1-N1	2.114(4)	Cu1-N6	1.9580(17)
Cr1-N2	2.004(4)	Cu1-N1	1.9586(18)
Cr1-01	1.997(3)	Cu1-01	1.9713(14)
Cr1-02	1.972(3)	Cu1-N7	2.0143(17)
Cr1-N5	2.001(4)	Cu1-N5	2.3797(17)
Cr1-02	1.962(3)		
01-Cr1-N5	91.88(15)	01-Cu1-N1	99.45(6)
01-Cr1-02	89.74(13)	01-Cu1- N5	92.80(6)
01-Cr1-02	101.56(13)	01-Cu1-N6	78.56(6)
01-Cr1-N1	92.13(14)	01-Cu1-N7	156.90(7)
02-Cr1-N2	174.60(16)	N1-Cu1- N5	96.33(7)
02-Cr1-01	101.56(13)	N1-Cu1-N6	160.03(7)
02-Cr1-N2	96.53(14)	N1-Cu1-N7	96.18(7)
02-Cr1-N5	171.79(15)	N6-Cu1- N5	103.60(6)

N6-Cu1-N7

N7-Cu1-N5

80.93(7)

102.31(6)



Fig. 2. View of hydrogen bonding interactions in (1).



Fig. 3. Two-dimensional slabs parallel with bc found in (1).



Fig. 4. Crystal structure representation of the polymeric complex [Cu(L)(N3)]_n (2).

are arranged in a terminal mode and are quasi-linear [N5–N6–N7; 160.6(10)°]. The dinuclear units interact via strong N–H \cdots N

Table 4Selected hydrogen bonding parameters in complexes 1 and 2.

D−H···A	d(D-H) (Å)	$d(H \cdot \cdot \cdot A)$ (Å)	$d(D \cdots A)$ (Å)	$(D-H\cdot\cdot\cdot A)$ (°)
Complex 1				
N4-H2···N3 ⁱ	0.92	2.07	2.975(7)	165
N4-H4···N7 ⁱⁱ	0.87	2.20	2.995(7)	152
N4−H4…N8 ⁱⁱ	0.87	2.20	3.065(7)	173
C2−H15···N8 ⁱⁱⁱ	0.89	2.40	3.171(7)	146
Complex 2				
N4-H1N4···01 ^{iv}	0.88	1.97	2.830(2)	165
N4-H2N4···N3 ^v	0.83	2.25	3.064(3)	166
C2−H2···N7 ^{iv}	0.93	2.50	3.324(3)	147
$C2-H2\cdots Cg(1)^{iv}$	0.93	2.76	3.672(2)	167

Symmetry codes: (i) -x + 2, -y, -z + 1; (ii) x + 1/2, -y + 1/2, z - 1/2; (iii) -x + 3/2, y + 1/2, -z + 3/2; (iv) x, -y + 3/2, z - 1/2; (v) -x, -y + 1, -z.

hydrogen bonds, namely N4–H2···N3 and N4–H4···N7(N8) and these H-bonding interactions expand the structure along the *b* and c directions and caused two-dimensional slabs parallel with *bc* for structure of this complex (Figs. 2 and 3).

3.3.2. Structure of $[Cu(L)(N3)]_n(2)$

The structure of complex 2 is depicted in Fig. 4 and the crystal data and structure refinement of 2 are summarized in Table 2. Single X-ray crystal analysis revealed a Cu(II) polynuclear complex forming 1D chain along c axis (Fig. 5) with $Cu \cdots Cu$ separation 6.205 Å. The azide ligands located on each Cu(II) center as terminal position. In 2, such as shown in 1, the Schiff base ligand is deprotonated and coordinated to Cu(II) center as a monoanionic ligand as also confirmed by the IR spectra data. The Cu(II) center is penta-coordinated with a distorted square pyramid geometry. The basal plane is formed by the nitrogen atoms of pyridyl and azometine (N6 and N7), the oxygen of the semicarbazone NNO chelating set (O1), and the nitrogen of the azide ligand (N1), the nitrogen atom from the adjacent Schiff base ligand (N5) is placed in an apical vertex at a higher distance [N5-Cu, 2.3797(17) Å]. The Cu1-N5 covalent bond connects the complex to the 1D chains in a zig-zag way (Fig. 5). The angle of two planes of the two adjacent ligands is 74.42(6)° and the value 103.60(6)° for the N6-Cu-N5 reflects this fact. The geometry around the Cu(II) center is close to square pyramidal with τ = 0.05, [τ = [$\beta - \alpha$]/60], where β and α are two largest angles around the central atom; τ is 0 and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively [50-54]. The coordination polyhedron around Cu(II) may be described as an axially elongated square pyramid with the Cu(1)-N(6), Cu(1)-N(7), Cu(1)-O(1) and Cu(1)-N(1) basal in which distances are 1.9580(17), 2.0143(17), 1.9713(14) and 1.9586(18) Å, respectively and the Cu(1)-N(5) axial distance is 2.3797(17) Å, and they



Fig. 5. View of 1D chains in a zig-zag way in (2).



Fig. 6. View of hydrogen bonding interactions in (2).



Fig. 7. The two-dimensional expansion of (2) with H-bonds via azide linkages.

are in good agreement with those previously reported in the literature [52–54]. Detailed information about bond lengths and angles in the copper coordination environment can be found in Table 3. As observed in the **1**, the chelate bite angles in the two five-membered rings are also close [O1–Cu1–N6 is 78.56(6)° and N6–Cu1–N7 is 80.93(7)°]. Azide ions located in terminal positions and are quasi-linear [N1–N2–N3; 176.5(2)°]. There are strong N–H…N hydrogen bonding interactions between the zig-zag chains (for more information see Table 4), namely N4–H2N4…N3 hydrogen bond which are relating the chains together and expand the structure

Table 5

The antibacterial activity of HL and $\boldsymbol{1}$ and $\boldsymbol{2}$ (MIC in $\mu g/mL).$

in two dimensions (Figs. 6 and 7) and N4–H1N4…O1 hydrogen bond, which connects the chains into 3D networks.

3.4. Antimicrobial screening

The antimicrobial screenings of the free ligand and the complexes were tested for their effect on certain bacteria and fungus. The minimum inhibitory concentration (MIC) values for the HL, 1 and 2 are summarized in Table 5. Study of MIC values, reveals that the Schiff base HL has a weak activity against *B. subtilis* and fungals C. kefyr, C. krusei. In complex 1, virtually no activity against all of tested cases was found, due to lower electronegativity and small atomic radius of Cr(III) center as reported in literature [55,56]. The complex **2** has the better activity in contrast with HL and **1**, especially against Gram positive and Gram negative bacteria and C. kefyr. Current studies reveal that higher electronegativity and large atomic radius decreases the effective positive charges on the metal complex molecules and it results to higher antimicrobial activity [11,19-21]. By comparing the MIC values of the synthesized compounds with MIC values of standard drugs, it is concluded that the HL, 1 and 2 have not strong activity.

3.5. Electrochemistry

It is evident from the cyclic voltammogram of the ligand that HL is electroactive over a range from 1.5 to -2 V in DMSO solvent [57–58]. There are two ligand-centered reductions at potentials -1.1 V and -1.83 V and one oxidation observed at 0.90 V, all of these are attributed to the pyridine ring of ligand. The cyclic voltammogram of the azide displays only an irreversible oxidation at the potential 0.85 V.

3.5.1. Electrochemistry of the compounds 1 and 2

The complex **1** displays oxidation wave at -1.05 and one reduction wave at -1.25 V these waves are related to reversible redox of Cr(III)/Cr(II). The cyclic voltammogram of complex **2** displays four oxidation waves in potentials 1.03, 0.80, 0.05 and -0.11 V and two reduction waves in 0.02 and -0.35 V. The two irreversible oxidation waves at 1.03 and 0.80 V are related to oxidation of HL and azide ligands, respectively. By comparing the cyclic voltammogram of compound **2** with of HL and azide, it is demonstrated that both the oxidation waves are shifted to lower potentials due to coordination to the metal center. Also the compound **2** displays two reversible redox waves. The oxidation and reduction waves at 0.05 and 0.02 V respectively are related to reversible redox of Cu(II)/Cu(I). Another oxidation and reduction waves at -0.11 and -0.35 V are due to reversible redox of Cu(I)/Cu(0).

4. Conclusion

Two azide complexes $[Cr(L)(N_3)(OCH_3)]_2$ (1) and $[Cu(L)(N_3)]_n$ (2) and HL [HL: pyridine 2-carbaldehyde semicarbazone], have been synthesized and characterized with FT-IR, UV–Vis spectral studies and single crystal X-ray diffraction analysis. The results of

Compound	Bacillus subtilis	Staphylococcus aureus	Escherichia coli	Erwinia carotovora	Candida kefyr	Candida krusei	Aspergillus niger
HL	625	1250	1250	1250	625	625	1250
Complex 1	>2500	>2500	>2500	>2500	>2500	>2500	>2500
Complex 2	312	312	312	312	312	625	625
*Gentamicin	4	8	8	8	-	-	-
*Amphotricin B	-	-	-	-	4	4	16
DMSO	-	-	-	-	-	-	-

*Gentamicin is used as the standard. MIC (µg/mL) minimum inhibitory concentration, i.e. the lowest concentration to completely inhibit the bacterial growth. *Amphotricin B is used as the standard. MIC (µg/mL) minimum inhibitory concentration, i.e., the lowest concentration to completely inhibit the fungal growth. single crystal X-ray diffraction revealed a distorted octahedral geometry for **1**, and a square pyramidal geometry with $\tau = 0.05$ for **2**. Complex **1** is a dinuclear complex with two methoxy bridging groups and also an azide ligand in a terminal mode is coordinated to each Cr(III) center. These azide terminal ligands are linking the dinuclear units to other dinuclear units via hydrogen bonding interaction into two-dimensional slabs parallel with *bc*. Complex **2** is a coordination polymer with 1D zig-zag chains, also an azide ligands are linking the zig-zag chains to cu(II) center. These azide ligands are linking the zig-zag chains to gether via hydrogen bonding interactions creating 2D network for this complex. The antimicrobial screening data revealed that the HL and new synthesized complexes didn't demonstrate strong activity in comparison to the standard drugs. The electrochemical studies demonstrated that HL, **1** and **2** are electrochemically active.

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Appendix A. Supplementary material

CCDC 870714 and 870715 contain the supplementary crystallographic data for Clusters **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2012.08.027.

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