



## **Synthesis, Antimicrobial and Thermal Activities of Co(II), Ni(II), Cu(II) Azo-Thiazole Complex Dyes and Their Application on Polyester Fabrics**

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### **ABSTRACT**

*4-((2-Amino-4-pyridin-3-yl)thiazol-5-yl)diazanyl)-5-hydroxynaphthalene-2,7-disulfonic acid and its Cu(II), Co(II) and Ni(II) complexes have been synthesized, characterized and applied on polyester fabrics. The ligand acts as monobasic bidentate for all complexes via deprotonated OH and nitrogen atom of the azo group. The complexes have tetrahedral structure except Cu (II) has an octahedral geometry. The color yield of the dyes furnished over fiber was found to be moderate to good. In addition; the synthesized dyes were screened for their antimicrobial activities against some Gram positive, Gram negative bacteria and fungi.*

**Keywords:** Azo thiazole dyes, Color fastness, Metal complex azo dyes, Thermal activity.

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### **INTRODUCTION**

Multidentate ligands are extensively used in coordination chemistry, since they can be applied in the construction of new frameworks with interesting properties [1-4]. Thiazoles have attracted much attention as ligands due to their synthetic feasibility and their incorporation into variety of therapeutically active agents. They represent a wide range of biological potencies including antibacterial, antifungal, anti-HIV, ant hypertension, anti-inflammatory, anticancer, anticonvulsant, and antidepressant meanwhile [5–14]. Acid azo dyes and their metal complexes are the most important class of commercial dyes and represent more than half of industrial dyes [15–17]. They are usually yellow, red, orange, blue or green, depending on the exact structure of the molecule. They have found wide application in dyeing polyester, wool, polyamide fibers and blends of both these fibers [18]. Heterocyclic azo dyes play an important role in the development of coordination chemistry. The importance of these compounds may stem from their biological activity and analytical investigations [19]. Also, azo dyes and their metal complexes have been studied widely because of their excellent thermal and optical properties such as optical data storage photo switching, non-linear optics and photochromic materials [20, 21]. The present study report the synthesis of 4-((2-amino-4-pyridin-3-yl)thiazol-5-yl)diazanyl)-5-hydroxynaphthalene-2,7-disulfonate (HL) and its Co (II), Ni (II) and Cu (II) complexes to be applied on polyester fabrics.

## MATERIALS AND METHODS

Commercially available polyester fabrics were used for dyeing. Chemicals were obtained from Sigma-Aldrich and used without further purification. The solvents used were of spectroscopic grade.

Melting points were recorded on a Gallenkamp melting point apparatus and reported uncorrected. The elemental analyses of complexes were performed at the micro analytical center, Cairo University using Perkin-Elmer 240 CHN Elemental analyzer. Metal content was estimated using Inductive Coupled plasma (ICP) Perkin Elmer/Optima 7000 DV at Tanta University. Molar conductivities in  $10^{-3}$  M DMF were measured at room temperature (25 °C) using Conductance Bridge of the type 523 conductivity bridges. The Infrared spectra were recorded on a JASCO FT/IR-4100 Spectrophotometer within the range 4000–400  $\text{cm}^{-1}$  as KBr discs. The electronic absorption spectra were recorded using a Shimadzu UV-Vis 240 Spectrophotometer using 1.0 cm matched silica cell. The magnetic susceptibility of the solids was measured at room temperature using magnetic susceptibility balance (Johnson Matthey; 436 Devon Park Drive) employing the Gouy's method. The thermogravimetric analysis (TGA) of the samples were performed within the range 25–1000 °C using the PERKIN ELMER (STA 6000) simultaneous thermal analysis with heating rate (15 °C  $\text{min}^{-1}$ ) under nitrogen atmosphere. The  $^1\text{H}$  NMR spectra were recorded on a Bruker AC spectrometer (300 MHz) at 25 °C in DMSO- $d_6$  with TMS as an internal standard. Electron Spray Ionization (ESI) mass spectra were recorded on a Shimadzu LCMS-2010 eV Spectrometer or Bruker Daltonics Micro TOF-15 Focus. The ligand was prepared as previously reported [22].

### Synthesis

**Synthesis of 4-((2-amino-4-(pyridin-3-yl) thiazol-5-yl) diazenyl)-5-hydroxynaphthalene-2, 7-disulfonate (HL):** A solution of sodium nitrite (0.9 g, 1.27 mmol,) in water (10 mL) was gradually added to a cold solution (0–5 °C) of 4-amino-5-hydroxynaphthalene-2,7-disulfonic acid (HA) (6.94 g, 1.37 mmol,) in conc. HCl (4 mL). The diazonium salt obtained was added with continuous stirring to a cold (0–5 °C) of 2-amino-4-(pyridin-3-yl)thiazole (1.5 g, 8.5 mmol,) in ethanol (42 mL) containing sodium acetate (3.4 g, 3.6 mmol,). The reaction mixture was stirred at 0 °C for 2 h. The colored formed solid was filtered, washed with water, dried and crystallized from ethanol to give the pure crystals (Scheme 1).

Product is 75% yield and purple crystals; m.p. 263–265 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 5.22 (s, exch., 2H,  $\text{NH}_2$ ), 5.87 (s, exch., 1H, OH), 7.81–9.11 (m, 8H, Ar-H), 14.17 (s, 2H,  $\text{SO}_3\text{H}$ ). IR (KBr)  $\nu$ : 3475 (OH), 3053 (Ar-H), 2920 (aliph-H), 1636 (C=N), 1503 (N=N), 1219 (C-O), 810 (C-S-C)  $\text{cm}^{-1}$ ; ESI-MS 507. Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}_7\text{S}_3$  (507.52): C, 40.60; H, 2.58; N, 13.80; S, 18.95; Found: C, 41.99; H, 1.74; N, 13.11; S, 17.12.

**General procedure for synthesis of the complexes 1-3:** 4-((2-Amino-4-(pyridin-3-yl) thiazol-5-yl) diazenyl)-5-hydroxynaphthalene-2,7-disulfonate (HL) (0.253 g, 0.5 mmol,) was dissolved in absolute ethanol (20 mL), then (0.5 mmol) of metal acetate in absolute ethanol (10 mL) was added dropwise with few drops of triethylamine and then refluxed for 10 h. The solid obtained was filtered, washed several times with methanol and ether and then dried in air. The reaction is shown in Scheme 2.

**Complex 1:** Product is 56% yield and dark purple crystals: m.p. over 360 °C. IR (KBr)  $\nu$ : 3475 (OH), 3066 ( $\text{NH}_2$ ), 1645 (C=N), 1518 (N=N), 1551 and 1391 (acetate), 1185 (C-O), 567 (Co-O), 462 (Co-N)  $\text{cm}^{-1}$ ; ESI-MS 741. Anal. Calcd for  $\text{C}_{22}\text{H}_{29}\text{CoN}_5\text{O}_{14}\text{S}_3$  (742.62): C, 35.58; H, 3.94; N, 9.43; S, 12.95; Co, 7.94; Found: C, 36.88; H, 4.98; N, 10.79; S, 13.94; Co, 8.99.

**Complex 2:** Product is 62% yield and dark purple crystals, m.p. over 360 °C. IR (KBr):  $\nu$ : 3475 (OH), 3065 ( $\text{NH}_2$ ), 1636 (C=N), 1520 (N=N), 1551 and 1373 (acetate), 1200 (C-O), 564 (Ni-O), 469 (Ni-N)  $\text{cm}^{-1}$ .

<sup>1</sup>; ESI-MS 661. Anal. Calcd for C<sub>20</sub>H<sub>19</sub>N<sub>5</sub>NiO<sub>11</sub>S<sub>3</sub> (660.28): C, 36.38; H, 2.90; N, 10.61; S, 14.57; Ni, 8.89; Found: C, 37.99; H, 3.28; N, 11.65; S, 16.54Ni, 8.72,

**Complex 3:** Product is 51% yield and Dark purple crystal, m.p. over 360°C. IR (KBr):  $\nu$ : 3475 (OH), 3058 (NH<sub>2</sub>), 1637 (C=N), 1468 (N=N), 1540 and 1387 (acetate), 1196 (C-O), 574 (Cu-O), 460 (Cu-N) cm<sup>-1</sup>; ESI-MS 684. Anal. Calcd for C<sub>20</sub>H<sub>21</sub>CuN<sub>5</sub>O<sub>12</sub>S<sub>3</sub> (683.15): C, 35.16; H, 3.10; N, 10.25; S, 14.08 Cu, 9.30; Found: C, 36.39; H, 4.15; N, 11.75; S, 15.23 Cu, 8.78.

**Molecular modeling studies:** An attempt to gain a better insight on the molecular structure of metal complexes, geometric optimization and conformational analysis has been performed using MM<sup>+</sup> force field as implemented in hyperchem 8.0 [23].

**Dying applications:** All applications and fastness properties of dye stuffs have been performed at Misr Spinning and Weaving Company, Central Q.C. Laboratories, Mehalla El-Kubra, Egypt. The synthesized dyes were applied to polyester fabrics and the dyeing procedures were carried out according to the reported procedures<sup>24</sup>. A dispersion of the dye was produced by dissolving the appropriate amount of dye (100 mg) in water (100 ml) and added dropwise with stirring to the dye bath (liquor ration 20:1) containing Setamol WS (1 %; sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The pH of the dye bath was adjusted to 5.5 using aqueous acetic acid and the wetted-out polyester fabrics (5 g) were added. Dyeing was performed by raising the dye bath temperature to 130 °C at a rate of 3°C min<sup>-1</sup> Anal. Calcd Anal. Calcd, holding at this temperature for 60 min and rapid cooling to 50°C. The dyed fabrics was rinsed with cold water and reduction cleared (1 g dm<sup>-3</sup> sodium hydroxide, 1 g dm<sup>-3</sup> sodium hydrosulfite), 10 min, 80°C. The samples were rinsed with hot and cold water and finally air-dried.

**Fastness determination:** Color fastness to light, washing, perspiration, and rubbing of the prepared dyes on cotton fabrics were studied using standard methods for the assessment of color fastness of textile [24]. The obtained results were collected in table 3.

**Fastness to washing:** The test assessed using the lounder-o-metersponsored by the American Association of Textile Chemists and Colorists (A.A.T.C.C.). A test specimen (10 cm × 4 cm) of the dyed fiber is taken and samples (5 cm × 4 cm) of white cotton and polyester fibers were placed in the container of the washing machine, with the necessary amount of the soap solution (5 g L<sup>-1</sup>) previously heated to 50 °C. The specimen was rinsed twice in cold water for 10 min and squeezed, and finally the composite specimen is opened out and dried in air. The color alteration of the uncovered portion of the specimen and the staining of both undyed fabrics was assessed using the international Grey scale.

**Fastness to perspiration:** The test specimen (6 cm × 6 cm) is placed between two species of undyed fabrics (cotton and polyester) and sewed along one side to form the test specimen. Testing fabrics were immersed into the solution of pH 4 at room temperature for 30 min. The solution was poured off and the sample was placed between two plastic plates (7.5 cm × 6.5 cm) under a force of about 4.5 kg. The plates containing the composite samples are kept in an oven at 37 °C for 4 h. The specimen is then separated from the undyed samples. The colors alteration of dyed materials and staining of the samples were assessed using the international grey scale.

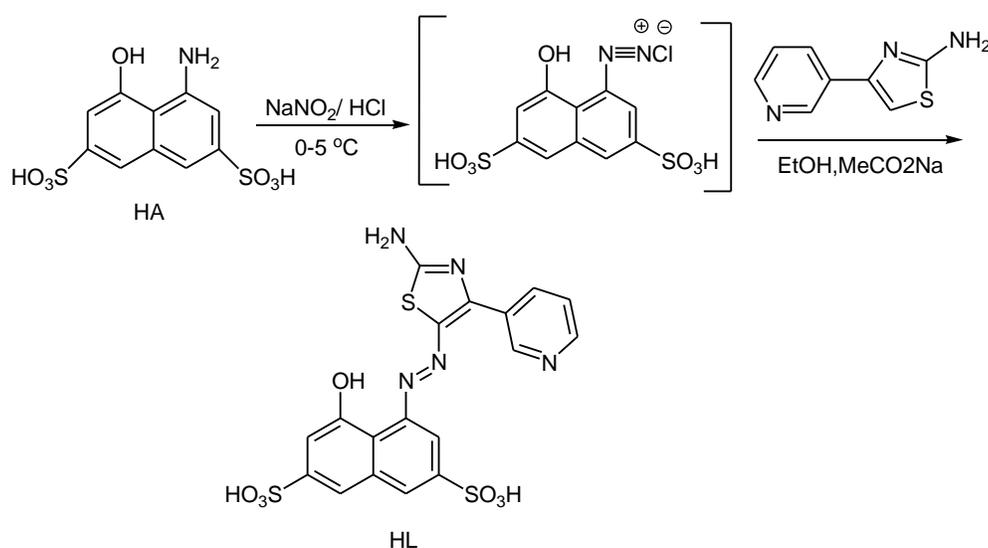
**Fastness to light:** The specimen of the dyed textiles are exposed, in a well ventilated exposure chamber to light from a xenon arc, along with dyed wool standards. The air temperature in the chamber was maintained at 30 °C. The effective humidity was maintained at 45 + 5%. The variation of light intensity over the area covered by specimen and standards should not exceed 20%. The samples and standards were exposed simultaneously under the same conditions for the same time. The samples were viewed in the

light from a day-light fluorescent lamp and given a degree in comparison with the relative to blue scale (1–8) standards of A.A.T.C.C.

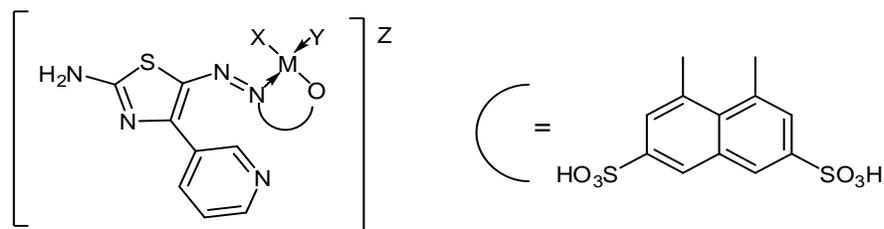
**Color measurement:** The colorimetric parameters of the dyed cotton fabrics were determined on a Reflectance Spectrophotometer (Gretag-Macbeth CE 7000a), equipped with a D65/10° source and barium sulphate as standard blank, and three repeated measurements average settings. The obtained results were recorded in table 4.

## RESULTS AND DISCUSSION

The synthesized metal chelates are colored and stable towards air and moisture. The analytical results of the complexes are consistent with the proposed molecular formulae and confirm the formation of 2:1 and 1:1 (M: L) complexes. The molar conductance in  $10^{-3}$  molar DMF solution values are 4.00, 3.00 and 1.10 ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) for complexes **1–3**, respectively. The observed molar conductance for all complexes reveals their non-electrolytic nature [25].



**Scheme 1.** Synthesis of 4-((2-amino-4-(pyridin-3-yl)thiazol-5-yl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonate (HL).



No.	M	X	Y	Z
1	Co	MeCO <sub>2</sub>	EtOH	4 H <sub>2</sub> O
2	Ni	MeCO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O
3	Cu	MeCO <sub>2</sub>	3 H <sub>2</sub> O	0

**Scheme 2.** Proposed structure of complexes

**<sup>1</sup>H NMR spectra of ligand:** The broad exchangeable signals corresponding to NH<sub>2</sub> protons on addition of D<sub>2</sub>O resonated at 5.22 ppm. The phenolic proton appeared as a singlet at 5.87 ppm and the sulphonic proton appeared as a singlet at 14.17 ppm which both disappeared on addition of D<sub>2</sub>O. The aromatic protons appeared as multiplets within the range 7.81–9.11 ppm.

**ESI-mass spectra:** The mass spectra of HL and complex **1** showed molecular ion (ML<sup>+</sup>) peaks at *m/z* 507 and 742, respectively. Pseudo molecular ion (ML<sup>+1</sup>) peaks are observed at *m/z* 661.96 and 684.40 for complexes **2** and **3** respectively.

**Infrared spectra:** For ligand, the IR absorption band appeared at 1639 cm<sup>-1</sup> is due to the ν C=N and in the same region as for the complexes suggesting that the nitrogen atom of the C=N bond does not participating on the chelation. The ligand band appeared at 1503 cm<sup>-1</sup> assigned to ν N=N group that shifted to higher or lower wave numbers by 17–55 cm<sup>-1</sup> in the IR spectra of complexes suggesting that it coordinate to the metal ion. The antisymmetric (ν<sub>anti</sub>) and symmetric (ν<sub>sym</sub>) stretching vibrations of the acetate group appeared in the range 1551–1540 and 1391–1371 cm<sup>-1</sup>, respectively. The difference between ν<sub>asym</sub> and ν<sub>sym</sub> indicates a monodentate coordination of acetate group. The strong absorption band appearing at 1217 cm<sup>-1</sup> in the IR spectrum for free ligand is due to the ν C–O vibration. The involvement of the of the OH group in chelation is confirmed by the red and blue-shift of the ν C–O stretching band to the extent 17–55 cm<sup>-1</sup> in complexes. The new bands that appeared within the range of 534–526 and 474–468 cm<sup>-1</sup> can be assigned to ν M–O and ν M–N bands, respectively confirming the coordination of both oxygen and nitrogen atoms to the metal center within complexes. The presence of lattice and coordinated water or ethanol molecules in the structure of metal complexes was supported further by the appearance of broad bands within the range of 3475–3477 cm<sup>-1</sup> corresponding to OH of water or ethanol molecules.

**Thermogravimetric analysis (TGA):** The thermal decomposition behavior of the complexes was followed up to 1000 °C in dynamic nitrogen atmosphere. The thermal behavior of the metal complexes was explained on the basis of TGA technique. Complexes **1** and **2** decomposed within four successive steps. The first step of decomposition occurred at 30–93 and 30–81 °C (found: 8.57, 2.89 calcd. 9.69, 2.72%), respectively, due to the loss of lattice water. The second step appeared at 93–132 and 81–101 °C (found: 5.99, 3.26 calcd. 6.16, 2.72%), respectively, due to the loss of coordinated ethanol and water. The third step occurred at 132–342 and 101–282 °C (found: 7.83, 9.34 calcd. 7.94, 8.93%), respectively, as a result of acetate ion loss. The last step appeared at 342–664 and 282–800 °C (found: 71.42, 69.64 calcd. 72.42, 69.18%), respectively due to the ligand decomposition leaving the metal nitride as a final product. The Cu (II) complex **3** decomposed within three successive steps. The first step occurred within at 30–123 °C (found: 7.18%, calcd. 7.90%) due loss of coordinated water. The second step appeared at 123–313 °C (found: 8.40 calcd. 8.63%) due to loss of coordinated acetate. The third step occurred at 313–800 °C (found: 69.83%, calcd. 68.02%) due decomposition of organic moiety leaving behind the thermally stable divalent metal nitride.

The thermodynamic parameters of different decomposition processes of complexes namely, enthalpy (ΔH\*), entropy (ΔS\*) and free energy of the decomposition (ΔG\*) as well as the activation energy (E\*), order (n) and correlation coefficient (r) were evaluated graphically using Coats–Redfern [25] and given in table 1. Fig 1 represents the Coats-Redfern plots of the decomposition steps of metal complexes. Table 1 showed that kinetics of thermal decomposition stages for all complexes follow the first order kinetics. The values of ΔG\* increased for the subsequently decomposition stages due to increase in TΔS\* from one stage to another due to the structural rigidity of the remaining complex after the expulsion of one and more ligand as competed with the precedent complex, which require more energy. The positive values of ΔG\* suggested that the process was non-spontaneous. The positive ΔH\* values indicate that the decomposition processes are endothermic. The negative values of the activation entropies ΔS\* indicate a more ordered activated complex than the reactants and/or the reactions are slower than normal [26].

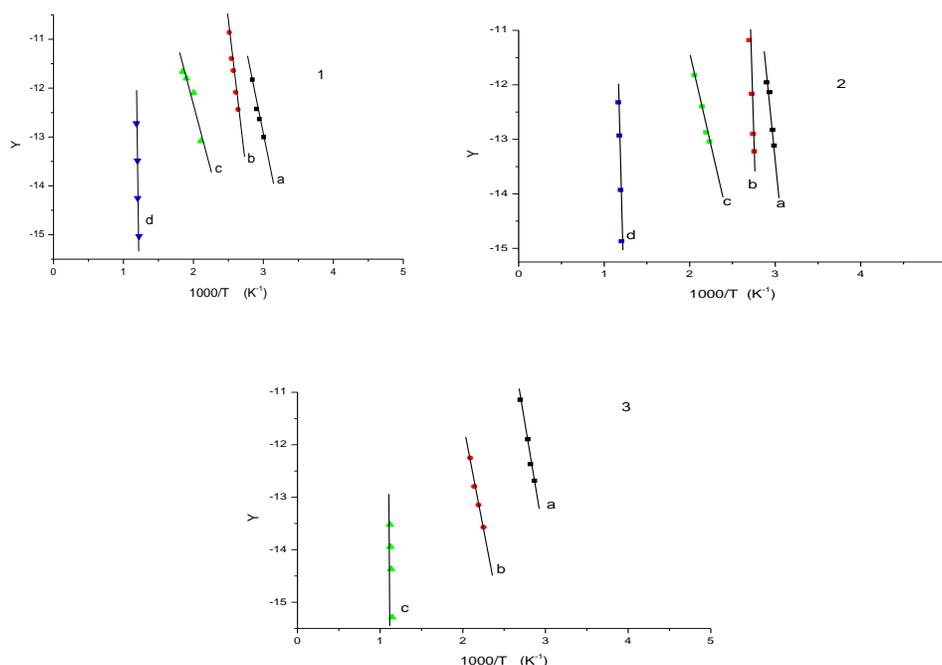
**Table 1** The activation parameters ( $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta G^*$ ) for decomposition of Co(II), Ni(II) and Cu(II) complexes

No	Step	T (K)	R	$E^*$ KJ/mol	$\Delta H^*$ KJ/mol	$-\Delta S^*$ KJ/mol K	$\Delta G^*$ KJ/mol
1	1	341.5	-0.9848	58.562	55.722	0.229	134.0373
	2	387.6	-0.9983	93.713	90.491	0.303	207.9588
	3	510.5	-0.9484	43.908	39.664	0.152	117.4695
	4	357.5	-0.9669	535.483	532.511	0.672	772.9154
2	1	338.5	-0.9719	115.672	112.858	0.393	246.067
	2 <sup>d</sup>	365.5	-0.9939	293.988	290.949	0.850	601.705
	3	463	-0.9939	59.867	56.018	0.189	143.5524
	4	839.5	-0.9918	536.873	529.893	0.677	1098.914
3	1	357.5	-0.9933	77.082	74.110	0.275	172.5423
	2	460.25	-0.9933	66.836	63.009	0.200	155.3341
	3	884	-0.9978	520.067	512.718	0.620	1061.611

**UV-Vis spectroscopic analysis and magnetic moment measurements:** The electronic absorption spectrum of Co(II) complex displayed two bands at 13037 and 17921  $\text{cm}^{-1}$  which assigned to  ${}^4A_2 \rightarrow {}^4T_1(F)$  and  ${}^4A_2 \rightarrow {}^4T_1(P)$  transition, respectively, due to the tetrahedral arrangement. The third transition due to  ${}^3A_2g \rightarrow {}^3T_2g$  would be out of the scale of the used spectrophotometer. The electronic absorption spectrum of Ni(II) complex showed two bands at 16977 and 19193  $\text{cm}^{-1}$  assignable to  ${}^3T_1(F) \rightarrow {}^3A_2$ ,  ${}^3T_1(F) \rightarrow {}^3T_1(p)$ , respectively, assuming the tetrahedral geometry around the Ni(II) ion. The spectrum for Cu(II) complex displayed a band at 21097  $\text{cm}^{-1}$  that assigned to  ${}^2E_g \rightarrow {}^2T_2g$  transition assuming octahedral geometry around the central Cu(II) ion.

The magnetic moment data of the solid complexes at room temperature showed that all complexes are paramagnetic. The magnetic moment value of Co(II) complex (4.76 BM) is higher than the theoretical spin only value of Co(II) complex refers to spin-orbital coupling. The magnetic moment values of Ni(II) and Cu(II) complexes (2.86 and 1.73 BM) are equal the theoretical spin only values. These values indicate tetrahedral structure for complexes **1** and **2** and octahedral geometry for complex **3**.

Based on the spectral data and magnetic moment values as well as the conductance values together with the data of elemental analysis, ICP and thermal analyses, the complexes can be formulated as in Fig. 1.

**Fig. 1.** Coats-Redfern plot for complexes

a) First step; b) second step; c) third step; d) fourth step;  $Y = [-\ln(1-\alpha)]/T^2$  for  $n=1$

**Molecular modeling:** Since our trials to obtain a single crystals of the metal complexes were unsuccessful so far, and in order to gain a better understanding of geometrical structures of the investigated complexes, molecular modeling studies have been done by means of Hyperchem program package. The details of bond lengths and bond angles per the 3D structure are given in Table S1 (Supplementary material). The optimized structures, with atom labeling scheme of the ligand and complexes **1–3** are represented in figs 2–5. Some selected bond distances and bond angles of metal complexes are listed in table 2.

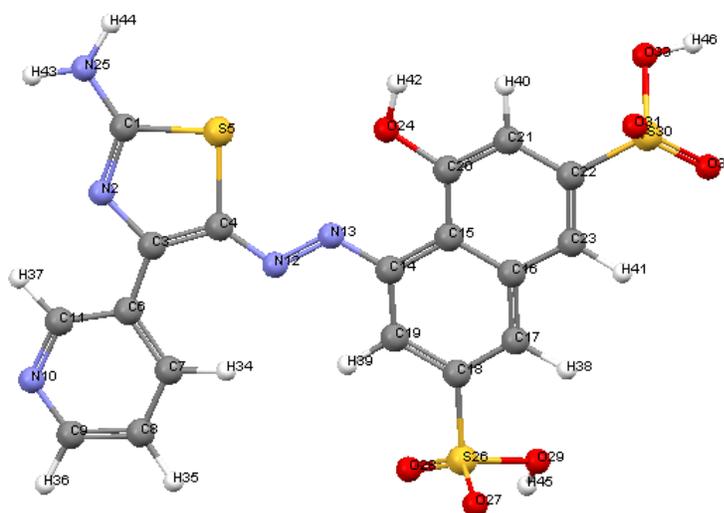
For complexes **1** and **2**, the coordination around the metal centers, involving O, N of ligand, acetate group, water and/or solvent molecules is distorted. The degree of distortion from ideal tetrahedral geometry is given by the minimum and maximum coordination angles around metal ions. For complexes **1** and **2**, the minimum angles are 109.47 and 109.47, respectively. The maximum angles are 111.58 and 111.53, respectively. From Table 2, it is clear that the bond angles are found to be within the normal ranges obtained from the crystal structure data [27]. The data revealed that, the degree of distortion from ideal tetrahedral geometry is very small. For complex **3** the copper ion is six coordinated suggesting octahedral geometry around the copper centre. The *cis* angles around the metal centre are 92.47, 89.97, 85.60 and 92.19°. While, the *trans*- angles around the metal centre are 175.81, 174.41 and 175.37. It is clear that the octahedral geometry is not much distorted. The obtained results are in good agreement with the experimental results.

**Table 2.** Some selected bond distances and bond angles of metal complexes

Bond	Angle (°)	Bond	Length (Å)
<b>Ligand</b>			
N13 N12 C14	120.24	N12N13	1.2489
N13C14C15	118.65	N13C14	1.2689
C14C15C20	122.31	C14C15	1.3539
C15C20O24	122.61	C15C20	1.3530
		C20O24	1.3614
<b>Complex 1</b>			
N13 N12 C14	120.91	N12N13	1.4500
N13C14C15	123.83	N13C14	1.3200
C14C15C20	125.81	C14C15	1.3678
C15C20O24	124.63	C15C20	1.4886
N13 Co26 O24	100.86	C20O24	1.3666
N13 Co26 O30	111.58	N13 Co26	1.8892
N13 Co26 O39	111.58	O24 Co26	1.8721
O24 Co26 O30	111.58	Co26 O30	1.8900
O24 Co26 O39	111.58	Co26 O39	1.8900
O30 Co26 O39	109.47		
<b>Complex 2</b>			
N13 N12 C14	120.91	N12N13	1.5000
N13C14C15	123.73	N13C14	1.3201
C14C15C20	125.69	C14C15	1.3670
C15C20O24	124.54	C15C20	1.4882
N13 Ni28 O24	101.08	C20O24	1.3663
N13 Ni28 O26	111.53	N13 Ni28	1.8799
N13 Ni28 O27	111.53	O24 Ni28	1.8622
O24 Ni28 O26	111.53	O26 Ni28	1.8800
O24 Ni28 O27	111.52	O27 Ni28	1.8799
O26 Ni28 O27	109.47		

Complex 3			
N13 N12 C14	120.00	N12N13	1.5000
N13C14C15	121.40	N13C14	1.3145
C14C15C20	122.80	C14C15	1.3452
C15C20O24	122.23	C15C20	1.4619
N13 Cu26 O24	87.08	C20O24	1.3639
N13 Cu26 O27	87.86	N13 Cu26	1.9122
N13 Cu26 O28	96.18	O24 Cu26	1.8970
N13 Cu26 O29	88.34	Cu26 O27	1.9011
N13 Cu26 O39	175.81	Cu26 O28	1.9012
O24 Cu26 O27	92.47	Cu26 O29	1.9012
O24 Cu26 O28	174.41	Cu26 O39	1.8980
O24 Cu26 O29	89.97		
O24 Cu26 O39	91.53		
O27 Cu26 O28	92.19		
O27 Cu26 O29	175.37		
O27 Cu26 O39	88.25		
O28 Cu26 O29	85.60		
O28 Cu26 O39	85.52		
O29 Cu26 O39	95.62		

**The dyeing properties on polyester fabrics:** Disperse new azo dyes, HL and its Co (II), Ni (II) and Cu (II) complexes were applied on polyester fabrics. HL was found to exhaust well on polyester fabrics to give dyeing with purple color. After treatment of these dye with cobalt, nickel and copper salts results in a marked bathochromic shift but without improvement of perspiration, washing and light fastness properties due to increase in size of dye molecules and the metal complex azodyes not formed inside the fabrics. The results of dyeing properties are summarized in Table 3 that showed good to excellent washing fastness suggesting that the dyes have affinity for the polyester fabrics. The perspiration fastness results were moderate to good and light fastness was fair to good.



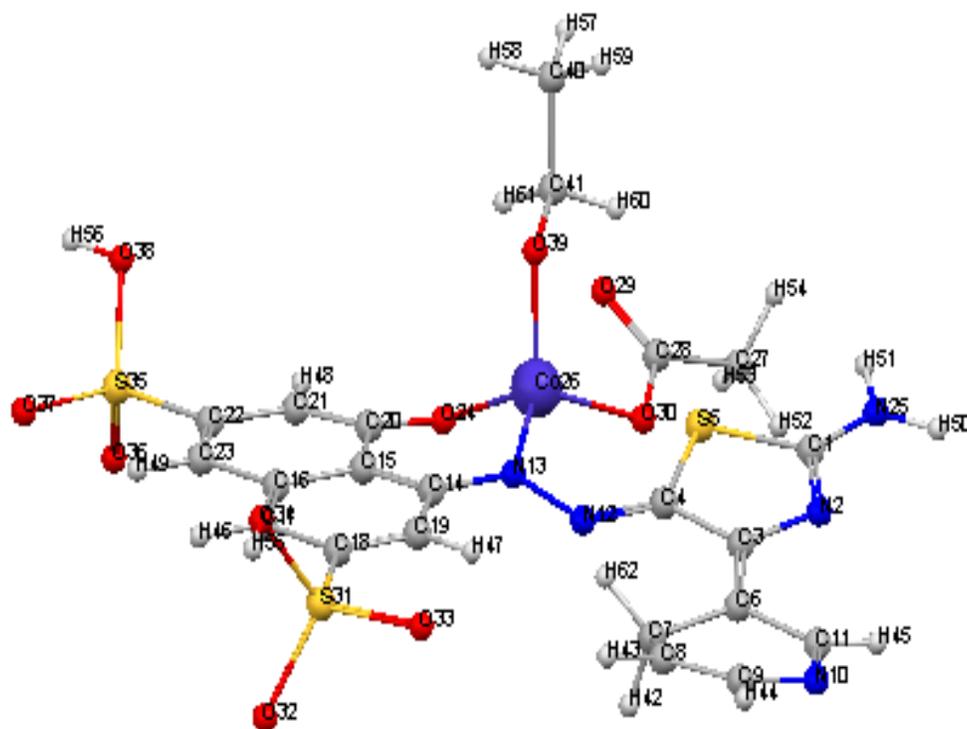


Fig. 3. Computational structure of complex 1

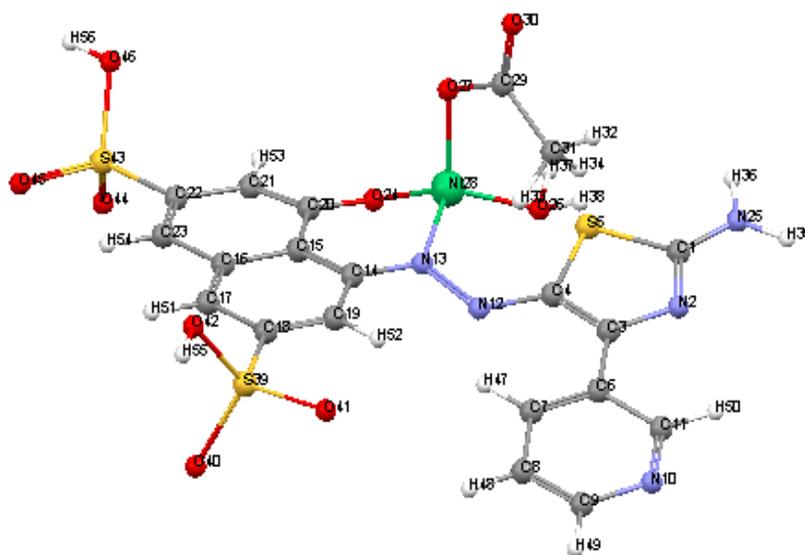


Fig. 4. Computational structure of complex 2

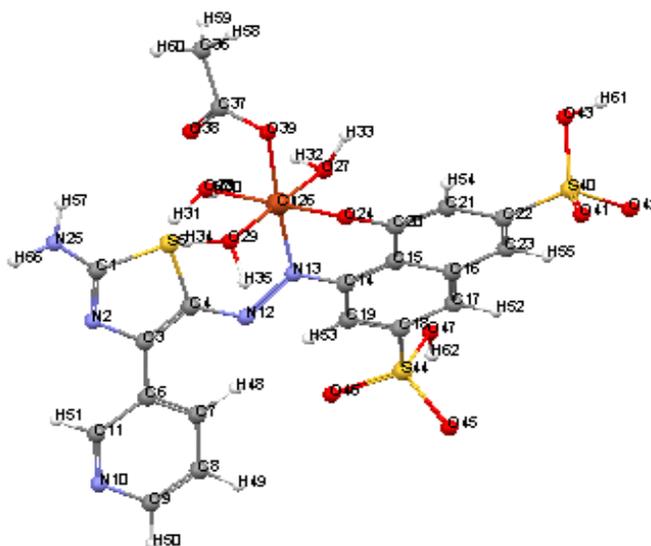


Fig. 5 Computational structure of complex 3

Table 3 Fastness properties of synthesized compounds on polyester fabrics<sup>a</sup>.

Dye No	Dye Color	Perspiration		Washing		Light
		acidic	alkali	alt	stain	
HL		4-5	4-5	5	4	6
1		4	4	4	4	5
2		3	3	3	4	4
3		4	4	3	4	4

**Color assessment:** The CIELAB coordinates, lightness ( $L^*$ ), ( $a^*$ ) value represents the degree of redness (positive) and greenness (negative) and ( $b^*$ ) represents the degree of yellowness (positive) and blueness (negative) were measured. The measured K/S values given by the reflectance spectrometer are directly correlated with the dye concentration on the dye substrate according to the Kubelkae Munk equation. The obtained results were depicted in table 4.

The color coordinate indicated that the ligand dye (HL) has good affinity with moderate to good brightness and depth to polyester fabrics. The color lightness value ( $L^*$ ) of dyes under investigation vary from 28.70–51.50. The dyes containing nickel is lighter than the others. On the other hand, K/S values for dyes vary from 2.15 to 21.70. Ligand dye is characterized by higher value compared to the metal complex dyes indicating that the color strength on polyester fabrics increased.

Table 4: Color of the dyes polyester fabrics

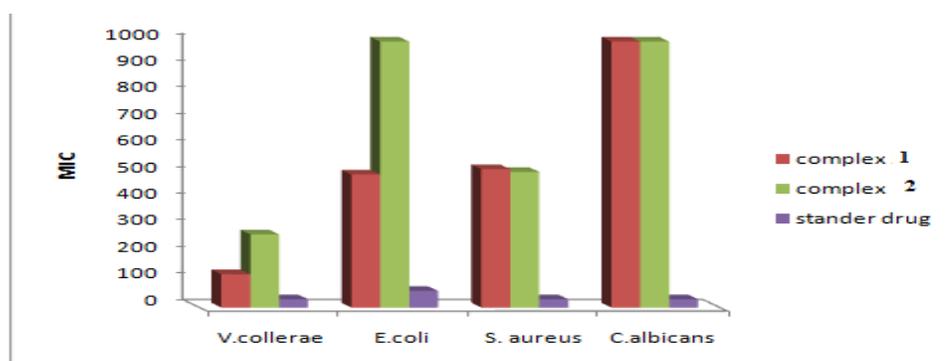
Dye No	$L^*$	$a^*$	$b^*$	R%	K/S
HL	37.20	16.10	-18.90	2.22	21.70
1	28.70	8.60	-14.60	4.40	10.38
2	51.50	13.70	-14.40	16.30	2.15
3	29.30	13.40	-15.50	3.46	13.60

<sup>a</sup> Rate for light fastness: 4–8 (acceptable), 1–3 (not acceptable); rate for different fastness: 3–5 (acceptable), 1–2 (not acceptable).

## APPLICATIONS

**Antimicrobial activity:** The antibacterial and antifungal activities of complexes were evaluated against *Staphylococcus aureus* (Gram positive bacterium), *Vibrio collerae*, *Escherichia coli*, and *Proteus vulgaris* (Gram negative bacteria) and *Candida albicans* (fungi). The results are presented in (Table 5). The data showed that the ligand and its complexes have significant inhibitory effect on *E. coli*. Complexes **1** and **2** have significant inhibitory effect on *Vibrio collerae*. On the other hand, they have no effect on *Proteus vulgaris* except complex **3**. Specific antimicrobial activity was exhibited by compounds **1** and **3** on *Staphylococcus aureus*. Also antimicrobial activity was exhibited by complexes **1** and **2** on *Candida albicans*. Complexes **1** and **2** gave excellent results against most of the tested organisms. The minimal inhibitory concentration (MIC) of some selected samples on the tested organisms is shown in fig. 6. Complexes **1** and **2** were effective on *Vibrio collerae* which showed MIC value of 125 and 275, respectively compared to the MIC for other organisms (500, 1000, 510, 520 and 1000).

**Antimicrobial activity:** The microorganisms used in this study included bacteria *Staphylococcus aureus* (Gram positive), *Vireo collerae*, *Escherichia coli*, and *Proteus vulgaris* (Gram negative) and *Candida albicans* (fungi). The strains were obtained from the culture collection of Bacteriology Laboratory (Bacteriology Unit, Department of Botany, Faculty of Science, Tanta University, and Tanta, Egypt). An aliquot of 0.1 mL of each bacterial strain was inoculated and spread on nutrient agar while 0.1 mL of the yeast was spread on sabaroud agar slopes. Antimicrobial activities of the synthesized compounds were tested *in vitro* using the cut- plug method according to Pridham et al. [25]. The assay plates were inoculated with 100 mL containing the diluted inoculums ( $10^7$  CFU mL<sup>-1</sup>) of each tested organism that were spread on the corresponding media. After solidification, the wells were made of dyes (10 mg) were dissolved in DMSO (1 mL) and inserted in the wells. Nutrient agar plated was incubated at 37 °C for 24 h while plates were incubated at 25 °C for 48 h. The inhibition zones around the wells were measured and the average based on reply was recorded. For reference drug 100 mg mL<sup>-1</sup> of Ampicillin was used as antibacterial and antifungal drugs.



**Fig 6.** Minimal inhibitory concentration (MIC) of the provided samples against test microorganisms (MIC)  $\mu\text{g mL}^{-1}$ ).

**Table 5.** Diameters of inhibition zones (mm) of newly synthesized compounds against different test bacteria and fungi on nutrient agar at 30°C after 24 h.

Comp. No	<i>V. collerae</i>	<i>E. coli</i>	<i>P. vulgaris</i>	<i>S. aureus</i>	<i>C. albicans</i>
HL	—	10	—	—	—
<b>1</b>	11	—	—	8	9
<b>2</b>	9	10	15	—	13
<b>3</b>	—	10	—	8	—
Ampicilline (standard drug)	—	30	10	8	18

**Table 6.** Minimal inhibitory concentration (MIC) of the provided samples against test microorganisms (MIC)  $\mu\text{g mL}^{-1}$ 

Comp.No	<i>Vibrio collerae</i>	<i>E.coli</i>	<i>Proteus vulgaris</i>	<i>Staphylococcus aureus</i>	<i>Candida albicans</i>
1	125	500	-	520	1000
2	275	1000	-	510	1000
St	31.25	62.5	62.5	31.25	31.25

All the dilutions of both samples and standards were performed by double fold dilution

## CONCLUSIONS

A series of novel azo dye ligand of 4-((2-amino-4-(pyridin-3-yl)thiazol-5-yl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonic acid and its Co(II), Ni(II) and Cu(II) complexes were synthesized in good yield. The molecular modeling studies indicated that metal complexes have tetrahedral structure except Cu (II) complex which had octahedral geometry. The synthesized ligand (HL) and its complexes were applied as disperse dyes for dyeing polyester fabrics. The light, washing and perspiration fastness of all patterns dyed show poor to good fastness properties. Also, the color coordinates indicate that the dyes have good affinity fair to good levelness brightness and depth to polyester fabrics. Complexes 2 and 3 gave excellent results as antimicrobial agents.

**Supplementary Information:** This is given in the following tables.

**Table S1** The details of bond angles of complexes

Complex 1	Complex 2	Complex 3
1 N2 C1 S5 110.93	1 N2 C1 S5 109.17	1 N2 C1 S5 109.17
2 N2 C1 N25 124.54	2 N2 C1 N25 125.42	2 N2 C1 N25 125.42
3 S5 C1 N25 124.54	3 S5 C1 N25 125.41	3 S5 C1 N25 125.42
4 C1 N2 C3 115.54	4 C1 N2 C3 115.28	4 C1 N2 C3 115.28
5 N2 C3 C4 113.67	5 N2 C3 C4 115.02	5 N2 C3 C4 115.02
6 N2 C3 C6 123.16	6 N2 C3 C6 122.49	6 N2 C3 C6 122.49
7 C4 C3 C6 123.17	7 C4 C3 C6 122.49	7 C4 C3 C6 122.49
8 C3 C4 S5 106.88	8 C3 C4 S5 108.58	8 C3 C4 S5 108.58
9 C3 C4 N12 126.56	9 C3 C4 N12 125.71	9 C3 C4 N12 125.71
10 S5 C4 N12 126.56	10 S5 C4 N12 125.71	10 S5 C4 N12 125.71
11 C1 S5 C4 92.98	11 C1 S5 C4 91.94	11 C1 S5 C4 91.94
12 C3 C6 C7 120.50	12 C3 C6 C7 120.33	12 C3 C6 C7 120.33
13 C3 C6 C11 120.50	13 C3 C6 C11 120.32	13 C3 C6 C11 120.33
14 C7 C6 C11 119.00	14 C7 C6 C11 119.35	14 C7 C6 C11 119.35
15 C6 C7 C8 109.47	15 C6 C7 C8 119.13	15 C6 C7 C8 119.12
16 C6 C7 H42 109.46	16 C6 C7 H47 120.44	16 C6 C7 H48 120.44
17 C6 C7 H62 109.46	17 C8 C7 H47 120.43	17 C8 C7 H48 120.44
18 C8 C7 H42 109.47	18 C7 C8 C9 119.81	18 C7 C8 C9 119.81
19 C8 C7 H62 109.47	19 C7 C8 H48 120.20	19 C7 C8 H49 120.19
20 H42 C7 H62 109.49	20 C9 C8 H48 120.00	20 C9 C8 H49 120.00
21 C7 C8 C9 121.45	21 C8 C9 N10 120.63	21 C8 C9 N10 120.64
22 C7 C8 H43 119.27	22 C8 C9 H49 119.69	22 C8 C9 H50 119.69
23 C9 C8 H43 119.28	23 N10 C9 H49 119.68	23 N10 C9 H50 119.68
24 C8 C9 N10 122.22	24 C9 N10 C11 120.85	24 C9 N10 C11 120.85
25 C8 C9 H44 118.89	25 C6 C11 N10 120.24	25 C6 C11 N10 120.24
26 N10 C9 H44 118.89	26 C6 C11 H50 119.89	26 C6 C11 H51 119.88
27 C9 N10 C11 121.42	27 N10 C11 H50 119.88	27 N10 C11 H51 119.88
28 C6 C11 N10 119.93	28 C4 N12 N13 120.00	28 C4 N12 N13 120.00
29 C6 C11 H45 120.07	29 N12 N13 C14 120.91	29 N12 N13 C14 120.00
30 N10 C11 H45 120.00	30 N12 N13 Ni28 120.91	30 N12 N13 Cu26 120.00
31 C4 N12 N13 120.00	31 C14 N13 Ni28 118.18	31 C14 N13 Cu26 120.00
32 N12 N13 C14 120.91	32 N13 C14 C15 123.73	32 N13 C14 C15 121.40

33 N12 N13 Co26 120.91	33 N13 C14 C19 116.11	33 N13 C14 C19 118.30
34 C14 N13 Co26 118.19	34 C15 C14 C19 120.15	34 C15 C14 C19 120.28
35 N13 C14 C15 123.83	35 C14 C15 C16 117.69	35 C14 C15 C16 118.97
36 N13 C14 C19 116.02	36 C14 C15 C20 125.69	36 C14 C15 C20 122.80
37 C15 C14 C19 120.13	37 C16 C15 C20 116.62	37 C16 C15 C20 118.22
38 C14 C15 C16 117.64	38 C15 C16 C17 121.42	38 C15 C16 C17 120.72
39 C14 C15 C20 125.81	39 C15 C16 C23 120.16	39 C15 C16 C23 119.27
40 C16 C15 C20 116.55	40 C17 C16 C23 118.40	40 C17 C16 C23 120.00
41 C15 C16 C17 121.44	41 C16 C17 C18 120.32	41 C16 C17 C18 119.90
42 C15 C16 C23 120.20	42 C16 C17 H51 119.84	42 C16 C17 H52 120.09
43 C17 C16 C23 118.34	43 C18 C17 H51 119.84	43 C18 C17 H52 120.00
44 C16 C17 C18 120.34	44 C17 C18 C19 119.33	44 C17 C18 C19 119.71
45 C16 C17 H46 119.83	45 C17 C18 S39 120.34	45 C17 C18 S44 120.14
46 C18 C17 H46 119.83	46 C19 C18 S39 120.33	46 C19 C18 S44 120.14
47 C17 C18 C19 119.29	47 C14 C19 C18 121.08	47 C14 C19 C18 120.37
48 C17 C18 S31 120.35	48 C14 C19 H52 119.46	48 C14 C19 H53 119.82
49 C19 C18 S31 120.35	49 C18 C19 H52 119.46	49 C18 C19 H53 119.82
50 C14 C19 C18 121.13	50 C15 C20 C21 119.47	50 C15 C20 C21 119.47
51 C14 C19 H47 119.44	51 C15 C20 O24 124.54	51 C15 C20 O24 122.23
52 C18 C19 H47 119.43	52 C21 C20 O24 115.19	52 C21 C20 O24 117.77
53 C15 C20 C21 119.48	53 C20 C21 C22 122.77	53 C20 C21 C22 121.80
54 C15 C20 O24 124.63	54 C20 C21 H53 118.61	54 C20 C21 H54 119.10
55 C21 C20 O24 115.10	55 C22 C21 H53 118.62	55 C22 C21 H54 119.10
56 C20 C21 C22 122.81	56 C21 C22 C23 120.63	56 C21 C22 C23 121.28
57 C20 C21 H48 118.59	57 C21 C22 S43 119.68	57 C21 C22 S40 119.35
58 C22 C21 H48 118.60	58 C23 C22 S43 119.69	58 C23 C22 S40 119.37
59 C21 C22 C23 120.61	59 C16 C23 C22 120.17	59 C16 C23 C22 119.85
60 C21 C22 S35 119.70	60 C16 C23 H54 120.00	60 C16 C23 H55 120.00
61 C23 C22 S35 119.70	61 C22 C23 H54 119.82	61 C22 C23 H55 120.15
62 C16 C23 C22 120.18	62 C20 O24 Ni28 110.05	62 C20 O24 Cu26 112.29
63 C16 C23 H49 119.82	63 C1 N25 H35 120.00	63 C1 N25 H56 120.00
64 C22 C21 H49 120.00	64 C1 N25 H36 120.00	64 C1 N25 H57 120.00
65 C20 O24 Co26 110.04	65 H35 N25 H36 120.00	65 H56 N25 H57 120.00
66 C1 N25 H50 120.00	66 H37 O26 H38 109.47	66 N13 Cu26 O24 87.08
67 C1 N25 H51 120.00	67 H37 O26 Ni28 109.47	67 N13 Cu26 O27 87.86
68 H50 N25 H51 120.00	68 H38 O26 Ni28 109.47	68 N13 Cu26 O28 96.18
69 N13 Co26 O24 100.86	69 Ni28 O27 C29 109.47	69 N13 Cu26 O29 88.34
70 N13 Co26 O30 111.58	70 N13 Ni28 O24 101.08	70 N13 Cu26 O39 175.81
71 N13 Co26 O39 111.58	71 N13 Ni28 O26 111.53	71 O24 Cu26 O27 92.47
72 O24 Co26 O30 111.58	72 N13 Ni28 O27 111.53	72 O24 Cu26 O28 174.41
73 O24 Co26 O39 111.58	73 O24 Ni28 O26 111.53	73 O24 Cu26 O29 89.97
74 O30 Co26 O39 109.47	74 O24 Ni28 O27 111.52	74 O24 Cu26 O39 91.53
75 C28 C27 H52 109.47	75 O26 Ni28 O27 109.47	75 O27 Cu26 O28 92.19
76 C28 C27 H53 109.48	76 O27 C29 O30 120.00	76 O27 Cu26 O29 175.37
77 C28 C27 H54 109.48	77 O27 C29 C31 120.00	77 O27 Cu26 O39 88.25
78 H52 C27 H53 109.46	78 O30 C29 C31 120.00	78 O28 Cu26 O29 85.60
79 H52 C27 H54 109.47	79 C29 C31 H32 109.47	79 O28 Cu26 O39 85.52
80 H53 C27 H54 109.48	80 C29 C31 H33 109.47	80 O29 Cu26 O39 95.62
81 C27 C28 O29 120.00	81 C29 C31 H34 109.48	81 Cu26 O27 H32 109.47
82 C27 C28 O30 120.01	82 H32 C31 H33 109.47	82 Cu26 O27 H33 109.47
83 O29 C28 O30 120.00	83 H32 C31 H34 109.47	83 H32 O27 H33 109.47
84 Co26 O30 C28 109.48	84 H33 C31 H34 109.47	84 Cu26 O28 H30 109.47
85 C18 S31 O32 109.47	85 C18 S39 O40 109.47	85 Cu26 O28 H31 109.47
86 C18 S31 O33 109.47	86 C18 S39 O41 109.47	86 H30 O28 H31 109.47
87 C18 S31 O34 109.47	87 C18 S39 O42 109.47	87 Cu26 O29 H34 109.47
88 O32 S31 O33 109.47	88 O40 S39 O41 109.47	88 Cu26 O29 H35 109.47
89 O32 S31 O34 109.47	89 O40 S39 O42 109.47	89 H34 O29 H35 109.47
90 O33 S31 O34 109.47	90 O41 S39 O42 109.47	90 C37 C36 H58 109.48
91 S31 O34 H55 109.47	91 S39 O42 H55 109.47	91 C37 C36 H59 109.47

Ligand	Complex 1	Complex 2	Complex 3
1 N2 C1 S5 108.64	1 N2 C1 S5 110.93	1 N2 C1 S5 109.17	1 N2 C1 S5 109.17
2 N2 C1 N25 126.67	2 N2 C1 N25 124.54	2 N2 C1 N25 125.42	2 N2 C1 N25 125.42
3 S5 C1 N25 124.69	3 S5 C1 N25 124.54	3 S5 C1 N25 125.41	3 S5 C1 N25 125.42
4 C1 N2 C3 116.44	4 C1 N2 C3 115.54	4 C1 N2 C3 115.28	4 C1 N2 C3 115.28
5 N2 C3 C4 116.74	5 N2 C3 C4 113.67	5 N2 C3 C4 115.02	5 N2 C3 C4 115.02
6 N2 C3 C6 115.49	6 N2 C3 C6 123.16	6 N2 C3 C6 122.49	6 N2 C3 C6 122.49
7 C4 C3 C6 127.76	7 C4 C3 C6 123.17	7 C4 C3 C6 122.49	7 C4 C3 C6 122.49
8 C3 C4 S5 107.60	8 C3 C4 S5 106.88	8 C3 C4 S5 108.58	8 C3 C4 S5 108.58
9 C3 C4 N12 128.59	9 C3 C4 N12 126.56	9 C3 C4 N12 125.71	9 C3 C4 N12 125.71
10 S5 C4 N12 123.78	10 S5 C4 N12 126.56	10 S5 C4 N12 125.71	10 S5 C4 N12 125.71
11 C1 S5 C4 92.98	11 C1 S5 C4 92.98	11 C1 S5 C4 91.94	11 C1 S5 C4 91.94
12 C3 C6 C7 124.95	12 C3 C6 C7 120.50	12 C3 C6 C7 120.33	12 C3 C6 C7 120.33
13 C3 C6 C11 120.96	13 C3 C6 C11 120.50	13 C3 C6 C11 120.32	13 C3 C6 C11 120.32
14 C7 C6 C11 114.09	14 C7 C6 C11 119.00	14 C7 C6 C11 119.35	14 C7 C6 C11 119.35
15 C6 C7 C8 120.65	15 C6 C7 C8 109.47	15 C6 C7 C8 119.13	15 C6 C7 C8 119.13
16 C6 C7 H34 123.24	16 C6 C7 H42 109.46	16 C6 C7 H47 120.44	16 C6 C7 H47 120.44
17 C8 C7 H34 116.11	17 C6 C7 H62 109.46	17 C8 C7 H47 120.43	17 C8 C7 H47 120.43
18 C7 C8 C9 118.26	18 C8 C7 H42 109.47	18 C7 C8 C9 119.81	18 C7 C8 C9 119.81
19 C7 C8 H35 121.13	19 C8 C7 H62 109.47	19 C7 C8 H48 120.20	19 C7 C8 H48 120.20
20 C9 C8 H35 120.61	20 H42 C7 H62 109.49	20 C9 C8 H48 120.00	20 C9 C8 H48 120.00
21 C8 C9 N10 122.33	21 C7 C8 C9 121.45	21 C8 C9 N10 120.63	21 C8 C9 N10 120.63
22 C8 C9 H36 121.42	22 C7 C8 C9 119.27	22 C8 C9 H49 119.69	22 C8 C9 H49 119.69
23 N10 C9 H36 116.25	23 C8 C9 H43 119.28	23 N10 C9 H49 119.68	23 N10 C9 H50 119.68
24 C9 N10 C11 118.74	24 C8 C9 N10 122.22	24 C9 N10 C11 120.85	24 C9 N10 C11 120.85
25 C6 C11 N10 125.92	25 C8 C9 H44 118.89	25 C6 C11 N10 120.24	25 C6 C11 N10 120.24
26 C6 C11 H37 122.96	26 N10 C9 H44 118.89	26 C6 C11 H50 119.89	26 C6 C11 H51 119.88
27 N10 C11 H37 111.11	27 C9 N10 C11 121.42	27 N10 C11 H50 119.88	27 N10 C11 H51 119.88
28 C4 N12 N13 116.78	28 C6 C11 N10 119.97	28 C4 N12 N13 120.00	28 C4 N12 N13 120.00
29 N12 N13 C14 120.24	29 C6 C11 H45 120.07	29 N12 N13 C14 120.91	29 N12 N13 C14 120.91
30 N13 C14 C15 118.65	30 N10 C11 H45 120.00	30 N12 N13 N128 120.91	30 N12 N13 Cu26 120.00
31 N13 C14 C19 122.04	31 C4 N12 N13 120.00	31 C14 N13 N128 118.18	31 C14 N13 Cu26 120.00
32 C15 C14 C19 111.31	32 N12 N13 C14 120.91	32 N13 C14 C15 123.73	32 N13 C14 C15 121.40
33 C14 C15 C16 119.03	33 N12 N13 C026 120.91	33 N13 C14 C19 116.11	33 N13 C14 C15 118.30
34 C14 C15 C20 122.31	34 C14 N13 C026 118.19	34 C15 C14 C19 120.15	34 C15 C14 C19 119.27
35 N13 C15 C20 118.66	35 N13 C14 C15 123.83	35 C14 C15 C16 117.69	35 C14 C15 C16 117.69
36 C15 C16 C17 120.41	36 N13 C14 C19 116.02	36 C14 C15 C20 125.69	36 C14 C15 C20 122.80
37 C15 C16 C23 120.68	37 C15 C14 C19 120.13	37 C16 C15 C20 116.62	37 C16 C15 C20 118.22
38 C17 C16 C23 118.90	38 C14 C15 C16 117.64	38 C15 C16 C17 121.42	38 C15 C16 C17 120.72
39 C16 C17 C18 121.14	39 C14 C15 C20 125.81	39 C15 C16 C23 120.16	39 C15 C16 C23 120.00
40 C16 C17 H38 119.85	40 C16 C15 C20 116.55	40 C17 C16 C23 118.40	40 C17 C16 C23 120.00
41 C18 C17 H38 119.01	41 C15 C16 C17 121.44	41 C16 C17 C18 120.32	41 C16 C17 C18 119.90
42 C17 C18 C19 118.06	42 C15 C16 C23 120.20	42 C16 C17 H51 119.84	42 C16 C17 H52 120.09
43 C17 C18 S26 120.72	43 C17 C16 C23 118.34	43 C18 C17 H51 119.84	43 C18 C17 H52 120.00
44 C19 C18 S26 121.22	44 C16 C17 C18 120.34	44 C17 C18 C19 119.33	44 C17 C18 C19 119.71
45 C14 C19 C18 122.05	45 C16 C17 H46 119.83	45 C17 C18 S39 120.34	45 C17 C18 C23 120.00
46 C14 C19 H39 120.31	46 C18 C17 H46 119.83	46 C19 C18 S39 120.33	46 C17 C18 C23 120.00
47 C18 C19 H39 117.65	47 C17 C18 C19 119.29	47 C14 C19 C18 121.08	46 C19 C18 S44 120.14
48 C15 C20 C21 119.45	48 C17 C18 S31 120.35	48 C14 C19 H52 119.46	47 C14 C19 C18 120.37
49 C15 C20 O24 122.61	49 C19 C18 S31 120.35	49 C18 C19 H52 119.46	48 C14 C19 H53 119.82
50 C21 C20 O24 117.94	50 C14 C19 C18 121.13	50 C15 C20 C21 119.47	49 C18 C19 H53 119.82
51 C20 C21 C22 122.38	51 C14 C19 H47 119.44	51 C15 C20 O24 124.54	50 C15 C20 C21 119.47
52 C20 C21 H40 117.76	52 C18 C19 H47 119.43	52 C21 C20 O24 115.19	51 C15 C20 O24 122.23
53 C22 C21 H40 119.86	53 C15 C20 C21 119.48	53 C20 C21 C22 122.77	52 C21 C20 O24 117.77
54 C21 C22 C23 117.77	54 C15 C20 O24 124.63	54 C20 C21 H53 118.61	53 C20 C21 C22 121.80
55 C21 C22 S30 120.68	55 C21 C20 O24 115.10	55 C22 C21 H53 118.62	54 C20 C21 H54 119.10
56 C23 C22 S30 121.54	56 C20 C21 H48 118.59	56 C21 C22 C23 120.63	55 C22 C21 H54 119.10
57 C16 C23 C22 121.06	58 C22 C21 H48 118.60	57 C21 C22 S43 119.68	56 C21 C22 C23 121.28
58 C16 C23 H41 119.75	59 C21 C22 C23 120.61	58 C23 C22 S43 119.68	57 C21 C22 S40 119.35
59 C22 C23 H41 119.20	60 C21 C22 S35 119.70	59 C16 C23 C22 120.17	58 C23 C22 S40 119.37
60 C20 O24 H42 109.14	61 C23 C22 S35 119.70	60 C16 C23 H54 120.00	59 C16 C23 C22 119.85
61 C1 N25 H43 114.08	62 C16 C23 C22 120.18	61 C22 C23 H54 119.82	60 C16 C23 H55 120.00
62 C1 N25 H44 115.46	63 C16 C23 H49 119.82	62 C20 O24 N128 110.05	61 C22 C23 H55 120.15
63 H43 N25 H44 130.46	64 C22 C23 H49 120.00	63 C1 N25 H35 120.00	62 C20 C24 Cu26 112.29
64 C18 S26 O27 106.86	65 C20 O24 C026 110.04	64 C1 N25 H36 120.00	63 C1 N25 H56 120.00
65 C18 S26 O28 107.89	66 C1 N25 H50 120.00	65 H35 N25 H36 120.00	64 C1 N25 H57 120.00
66 C18 S26 O29 103.43	67 C1 N25 H51 120.00	66 H37 O26 H38 109.47	65 H56 N25 H57 120.00
67 O27 S26 O28 128.10	68 H50 N25 H51 120.00	67 H37 O26 N128 109.47	66 N13 Cu26 O24 87.08
68 O27 S26 O29 105.35	69 N13 C026 O24 100.86	68 H38 O26 N128 109.47	67 N13 Cu26 O27 87.86
69 O28 S26 O29 102.63	70 N13 C026 O30 111.58	69 N128 O27 C29 109.47	68 N13 Cu26 O28 96.18
70 S26 O29 H45 106.01	71 N13 C026 O30 111.58	70 N13 N128 O24 101.08	69 N13 Cu26 O29 88.34
71 C22 S30 O31 106.82	72 O24 C026 O30 111.58	71 N13 N128 O26 111.53	70 N13 Cu26 O39 175.81
72 C22 S30 O32 107.95	73 O24 C026 O39 111.58	72 N13 N128 O27 111.53	71 O24 Cu26 O27 92.47
73 C22 S30 O33 103.47	74 O30 C026 O39 109.47	73 O24 N128 O26 111.53	72 O24 Cu26 O28 174.41
74 O31 S30 O32 128.10	75 C28 C27 H52 109.47	74 O24 N128 O27 111.52	73 O24 Cu26 O29 89.97
75 O31 S30 O33 105.05	76 C28 C27 H53 109.48	75 O26 N128 O27 109.47	74 O24 Cu26 O39 91.53
76 O32 S30 O33 102.89	77 C28 C27 H54 109.48	76 O27 C29 O30 120.00	75 O27 Cu26 O28 92.19
77 S30 O33 H46 106.11	78 H52 C27 H53 109.46	77 O27 C29 C31 120.00	76 O27 Cu26 O29 175.37
	79 H52 C27 H54 109.47	78 O30 C29 C31 120.00	77 O27 Cu26 O39 88.25
	80 H53 C27 H54 109.48	79 C29 C31 H32 109.47	78 O28 Cu26 O29 85.60
	81 C27 C28 O29 120.00	80 C29 C31 H33 109.47	79 O28 Cu26 O39 85.52
	82 C27 C28 O30 120.01	81 C29 C31 H34 109.48	80 O29 Cu26 O39 95.62
	83 O29 C28 O30 120.00	82 H32 C31 H33 109.47	81 Cu26 O27 H32 109.47
	84 C026 O30 C28 109.48	83 H32 C31 H34 109.47	82 Cu26 O27 H33 109.47
	85 C18 S31 O32 109.47	84 H33 C31 H34 109.47	83 H32 O27 H33 109.47
	86 C18 S31 O33 109.47	85 C18 S39 O40 109.47	84 Cu26 O28 H30 109.47
	87 C18 S31 O34 109.47	86 C18 S39 O41 109.47	85 Cu26 O28 H31 109.47
	88 O32 S31 O33 109.47	87 C18 S39 O42 109.47	86 H30 O28 H31 109.47
	89 O32 S31 O34 109.47	88 O40 S39 O41 109.47	87 Cu26 O29 H34 109.47
	90 O33 S31 O34 109.47	89 O40 S39 O42 109.47	88 Cu26 O29 H35 109.47
	91 S31 O34 H55 109.47	90 O41 S39 O42 109.47	89 H34 O29 H35 109.47
	92 C22 S35 O36 109.47	91 S39 O42 H55 109.47	90 C37 C36 H58 109.48
	93 C22 S35 O37 109.47	92 C22 S43 O44 109.47	91 C37 C36 H59 109.47
	94 C22 S35 O38 109.47	93 C22 S43 O45 109.47	92 C37 C36 H60 109.47
	95 O36 S35 O37 109.47	94 C22 S43 O46 109.47	93 H58 C36 H59 109.47
	96 O36 S35 O38 109.47	95 O44 S43 O45 109.47	94 H58 C36 H60 109.47
	97 O37 S35 O38 109.47	96 O44 S43 O46 109.47	95 H59 C36 H60 109.47
	98 S35 O38 H56 109.47	97 O45 S43 O46 109.47	96 C36 C37 O38 120.00
	99 C026 O39 C41 109.47	98 S43 O46 H56 109.47	97 C36 C37 O39 120.00
	100 C41 C40 H57 109.47		98 O38 C37 O39 120.00
	101 C41 C40 H58 109.47		99 Cu26 O39 C37 109.47
	102 C41 C40 H59 109.47		100 C22 S40 O41 109.47
	103 H57 C40 H58 109.48		101 C22 S40 O42 109.47
			102 C22 S40 O43 109.47
			103 O41 S40 O42 109.47

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