Bull. Chem. Soc. Ethiop. **2020**, 34(2), 313-321.
ISSN 1011-3924
Printed in Ethiopia
DOI: https://dx.doi.org/10.4314/bcse.v34i2.9

SYNTHESIS AND CHARACTERIZATION OF NOVEL FOUR HETERODIMETALLIC MIXED METAL COMPLEXES OF 2,6-PYRIDINEDICARBOXYLIC ACID

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(Received July 4, 2019; Revised September 26, 2020; Accepted September 30, 2020)

ABSTRACT. Four novel hetero dimetallic mixed metal complexes of 2,6-pyridinedicarboxylic acid (H_2dipic), [Ni(H_2O)$_5$Co(dipic)$_2$] (**1**), [Co(H_2O)$_5$Co(dipic)$_2$][Ni(H_2O)$_5$Ni(dipic)$_2$][Co(dipic)(H_2O)$_3$] (**2**), [Cu(H_2O)$_5$Ni(dipic)$_2$]$_2$[Co(dipic)(H_2O)] (**3**) and [Ni(H_2O)$_5$Cu(dipic)$_2$]$_2$[Co(dipic)(H_2O)] (**4**) have been prepared and characterized by elemental, AAS, spectral (IR and UV-Vis), and thermal analyses, as well as by using magnetic measurement and molar conductivity techniques. The results indicate that metal ions coordinate with 2,6-pyridinedicarboxylate ions (dipic^{2-}) nitrogen atoms and carboxylate oxygen atoms of ligands. The mole ratio of dipic^{2-} and metal ions in the complexes have been determined to be 2:2 (Co, Ni) for **1**, 5:5 (3Co, 2Ni) for **2**, 5:5 (Co, 2Ni and 2Cu) for **3** and 5:5 (Co, 2Ni and 2Cu) for **4** according to the results of elemental analysis. The structures of **1-4** might be proposed as octahedral ([Cu(dipic)(H_2O)] unit for **2** square plane) according to results of spectroscopic analysis. The TG and DTA properties of compounds have been studied.

KEY WORDS: 2,6-Pyridinedicarboxylic acid, Mixed metal, Metal complex

INTRODUCTION

The metal complexes for pyridine-2,6-dicarboxylic acid (or dipicolinic acid, H_2dipic) and its deprotonated forms (Hdipic$^-$ and dipic^{2-}) show interesting structural features with various coordination modes [1], stabilization of unusual oxidation states [2] and insulin-mimetic effects [3, 4]. H_2DPC with Cu(II) ion commonly has one or two coordination modes [4]. In one coordination mode, a single planar DPC ligand associates in the equatorial plane of a metal cation with other ligands such as, H_2O or pyridine-based heterocycles [4, 5], which occupy the remaining sites. This leads to the formation of square pyramidal [4, 6-10] or octahedral coordination geometry [4, 10-12, 14]. In the second coordination mode, two perpendicularly coordinated planar dipicolinic molecules generate distorted octahedral coordination geometry [4, 9, 10, 11].

Among the diversity of 2,6-pyridinedicarboxlate complexes known, there are several examples of homodimetallic {[M(H_2O)$_5$M(dipic)$_2$].2H_2O (M = Co [12-20], Ni [21] or Cu [22, 23])} and heterodimetallic [{[M(H_2O)$_5$M'(dipic)$_2$].mH_2O {M/M' = Cu(II)/Co(II), Cu(II)/Ni(II), Cu(II)/Zn(II), Zn(II)/Co(II), Ni(II)/Co(II) [24]; Cu(II)/Ni(II), Cu(II)/Co(II), Cu(II)/Mn(II) [25]; Cu(II)/Co(II), Cu(II)/Ni(II), Cu(II)/Zn(II) [26]; Zn(II)/Cu(II) [27]; Cu(II)/Mn(II) [28]; m = 2 or 3} aqua compounds of the types and with potential applications in fields of aqueous chemistry, catalysis, biochemistry, as water-soluble drugs, magnetic materials, in bleaching and bactericidal compositions [12-14, 17, 22, 24].

In this study, four novel homodimetallic mixed metal complexes of H_2dipic, [Ni(H_2O)$_5$Co(dipic)$_2$] (**1**), [Co(H_2O)$_5$Co(dipic)$_2$][Ni(H_2O)$_5$Ni(dipic)$_2$][Co(dipic)(H_2O)$_3$] (**2**), [Cu(H_2O)$_5$Ni(dipic)$_2$]$_2$[Co(dipic)(H_2O)] (**3**) and [Ni(H_2O)$_5$Cu(dipic)$_2$]$_2$[Co(dipic)(H_2O)] (**4**) have been prepared and characterized by elemental analysis (CHNS), AAS, spectral (IR and UV-Vis.), and thermal analyses, as well as by using magnetic measurement and molar conductivity techniques.

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EXPERIMENTAL

General methods and materials

All chemicals used were analytical reagents and were commercially purchased from Aldrich. Elemental analyses for C, H and N were performed on Elementar Vario III EL and Co, Ni and Cu were detected with Perkin Elmer Optima 4300 DV ICP-OES. FT-IR spectra were recorded in the 4000-400 cm^{-1} region with Bruker Optics, Vertex 70 FT-IR spectrometer using ATR techniques. Thermal analyses were performed on Pelkin Elmer SII Exstar 6000 TG/DTA 6300 model using platinum crucible with 10 mg sample. Measurements were taken in the static air within a 30-900 ºC temperature range. The UV–Vis spectra were obtained for DMSO solution of the compounds (10^{-3} M) with a SHIMADZU UV-2550 spectrometer in the range of 200–900 nm. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific Magway MSB MK1 model magnetic balance by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. The molar conductance of the compounds were determined in water/ethanol (1:1) and in DMSO (10^{-3} M) at room temperature using a WTW Cond 315i/SET Model conductivity meter.

*Synthesis of **1-4***

A solution of 1 mmol (0.249 g) $Co(CH_3COO)_2.4H_2O$ and 2 mmol H_2dipic (0.334 g) in water (30 mL) with stirring at room temperature for two hours was added dropwise to the solution of 1 mmol (0.248 g) $Ni(CH_3COO)_2.4H_2O$ in water (20 mL) with stirring at room temperature for two hours to complete the reaction. On filtration the reaction mixture, the solution was kept at room temperature for two weeks to give brown amorphous solid for **1** (0.377 g, 70% yield).

A solution of 1 mmol (0.248 g) $Ni(CH_3COO)_2.4H_2O$ and 2 mmol H_2dipic (0,334 g) in water (30 mL) with stirring at room temperature for two hours was added dropwise to the solution of 1 mmol (0.249 g) $Co(CH_3COO)_2.4H_2O$ in water (20 mL) with stirring at room temperature for two hours to complete the reaction. On filtration the reaction mixture, the solution was kept at room temperature for two weeks to give brown amorphous solid for **2** (0.266 g, 50% yield).

A solution of 1 mmol (0.248 g) $Ni(CH_3COO)_2.4H_2O$ and 2 mmol H_2dipic (0.334 g) in water (30 mL) with stirring at room temperature for two hours was added dropwise to the solution of 1 mmol (0.200 g) $Cu(CH_3COO)_2.2H_2O$ in water (20 mL) with stirring at room temperature for two hours to complete the reaction. On filtration the reaction mixture, the solution was kept at room temperature for two weeks to give green amorphous solid for **3** (0.346 g, 65% yield).

A solution of 1 mmol (0.200 g) $Cu(CH_3COO)_2.2H_2O$ and 2 mmol H_2dipic (0.334 g) in water (30 mL) with stirring at room temperature for two hours was added dropwise to the solution of 1 mmol (0.248 g) $Ni(CH_3COO)_2.4H_2O$ in water (20 mL) with stirring at room temperature for two hours to complete the reaction. On filtration the reaction mixture, the solution was kept at room temperature for two weeks to give turquoise amorphous solid for **4** (0.400 g, 75% yield).

Suggested structures of the compounds (**1-4**) are shown in Figure 1.

Anal. calcd. for **1** ($C_{14}H_{16}CoN_2NiO_{13}$): C, 31.25%; H, 3.02%; Co, 10.98%, N, 5.25%; Ni, 10.85%; found: C, 31.26%; H, 3.00%; Co, 10.96%, N, 5.21%; Ni, 10.91%; for **2** ($C_{35}H_{41}Co_3N_5Ni_2O_{33}$): C, 31.03%; H, 3.00%; Co, 13.01%, N, 5.21%; Ni, 8.70%; found: C, 31.05%; H, 3.05%; Co, 13.06%, N, 5.17%; Ni, 8.67; for **3** ($C_{35}H_{37}Cu_3N_5Ni_2O_{33}$): C, 31.55%; H, 2.80%; Cu, 14.30%, N, 5.25%;Ni, 8.85%; found: C, 31.57%; H, 2.80%; Cu, 14.32%, N, 5.26%; Ni, 8.81; for **4** ($C_{35}H_{37}Cu_3N_5Ni_2O_{33}$): C, 31.56%; H, 2.82%; Cu, 14.35%, N, 5.21%; Ni, 8.80%; found: C, 31.57%; H, 2.80%; Cu, 14.32%, N, 5.26%; Ni, 8.81.

RESULTS AND DISCUSSION

The infrared spectral data of the starting compound (H_2dipic) and compounds **1-4** are given in Table 1. In the high frequency region, weak bands 3067-3098 cm^{-1} are attributed to the stretching vibrations of aromatic C-H for all compounds. There are also broad absorption bands at 3493-3474 cm^{-1}, which are attributed to the ν(OH) vibrations of water molecules for compounds **1-4**. The carboxylate groups for compounds H_2dipic and **1-4** exhibit strong carbonyl bands in the region of 1701-1456 cm^{-1}.

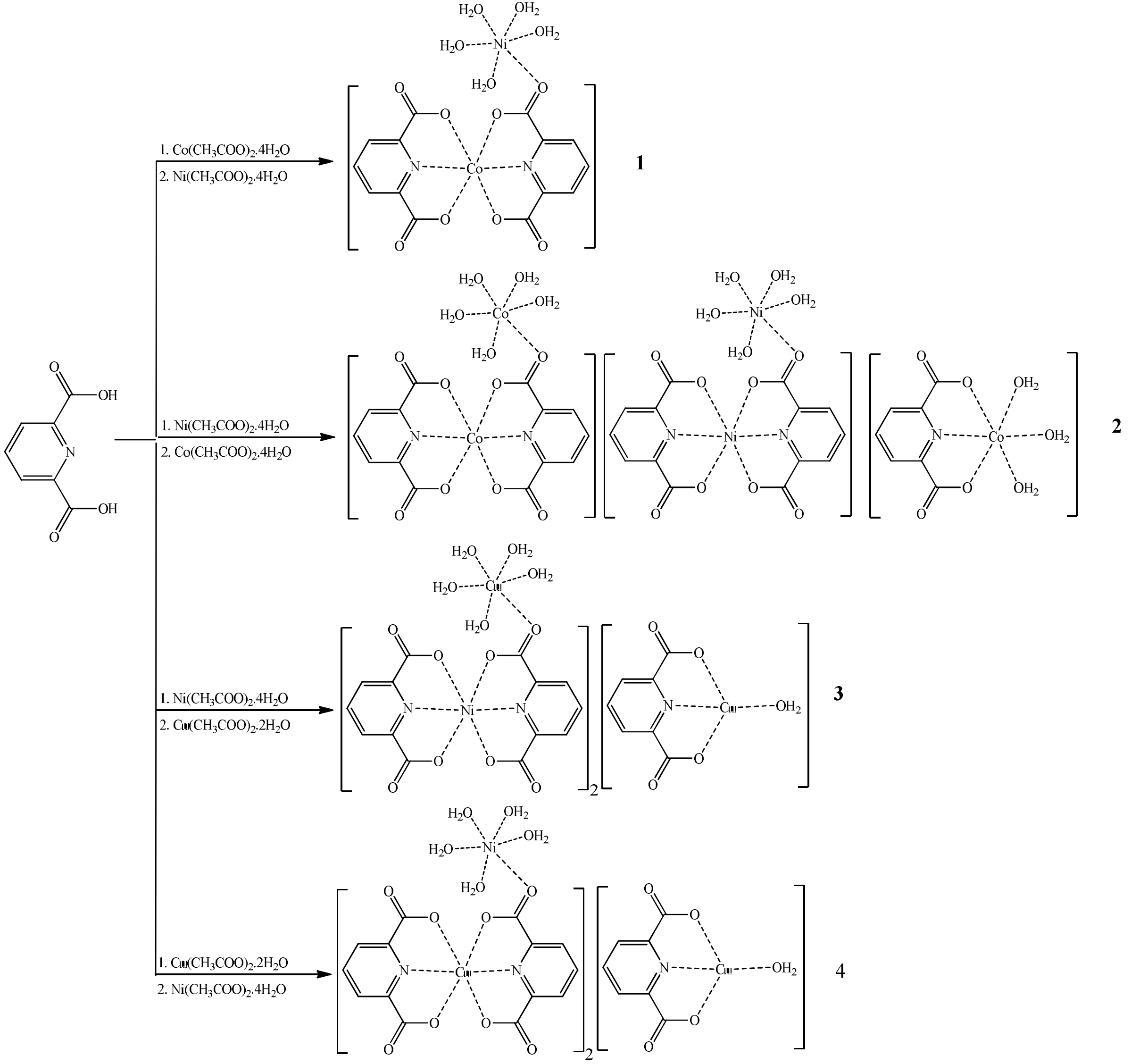

Figure 1. Syntheses of all compounds.

These bands are reflected by IR spectrum of the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations at 1701 and 1456 cm^{-1} for H$_2$dipic, 1615 and 1432, 1606 and 1486 cm^{-1} for **1**, 1620 and 1452, 1605 and 1487 cm^{-1} for **2**, 1615 and 1432, 1606 and 1486 cm^{-1} for **3**, and 1620 and 1422, 1605 and 1487 cm^{-1} for **4**. The differences ($\Delta\nu$) between the asymmetric and symmetric stretches of the carboxylate groups of 183 and 120 for **1**, 168 and 118 for **2**, 183 and 120 for **3** and 168 and 120 for **4** are which suggest monodentate and bridging, respectively, binding of the carboxylate group to the metal ion in all complexes [29]. The strong absorption bands in the region of 1595-1426 cm^{-1} are attributed to the ν(C=N) and ν(C=C) vibrations for all compounds. The C–O vibrations data for all compounds between 1369 and 1060 cm^{-1} as expected. The ring wagging vibrations of the pyridine groups are also observed in the 801-706 cm^{-1} region for compounds H$_2$dipic and **1-4**. The weak bands at 429-459 cm^{-1} and 595-551 cm^{-1} are from the M–N and M–O vibrations of the compounds **1-4** (Table 1).

Table 1. IR spectral data of **1-5** (cm^{-1}).

	H$_2$DPC	**1**	**2**	**3**	**4**
ν(OH)	2900(br)	3474(br)	3493(br)	3474(br)	3493(br)
ν(C-H)	3069(w)	3090(w)	3085(w)	3071(w)	3080(w)
ν(COO)*	1701(s) 1456(s)	1615(s) 1432(s)	1620(s) 1452(s)	1615(s) 1432(s)	1620(s) 1452(s)
ν(COO)**		1606(s) 1486(s)	1605(s) 1487(s)	1606(s) 1486(s)	1605(s) 1487(s)
ν(C=N) ν(C=C)	1574(s) 1415(s)	1595(s) 1577(s) 1563(s) 1432(s) 1429(s)	1590(s) 1587(s) 1533(s) 1452(s) 1426(s)	1595(s) 1577(s) 1563(s) 1432(s) 1429(s)	1590(s) 1587(s) 1533(s) 1452(s) 1426(s)
ν(C-O)	1333(s) 1299(s) 1080(s)	1369(s) 1284(s) 1074(s)	1359(s) 1274(s) 1070(s)	1360(s) 1280(s) 1060(s)	1359(s) 1274(s) 1085(s)
ν(py)	782(s)	762(s)	752(s)	775(s)	760(s)
ν(Co-O)	-	551(s)	555(s)	-	-
ν(Co-N)	-	436(w)	439(w)	-	-
ν(Ni-O)	-	591(s)	595(s)	591(s)	595(s)
ν(Ni-N)	-	459(w)	442(w)	438(w)	429(w)
ν(Co-O)	-	-	-	551(s)	555(s)
ν(Cu-N)	-	-	-	429(w)	430(w)

Abbreviations: w, weak; m, medium; s, strong; b, broad.

Figures 2-5 show the TG-DTG and DTA curves of compounds **1-4**, respectively, and thermal analyses results are given in Table 2. For all compounds (**1-4**), the first stage, an endothermic peak corresponds to the loss of water molecules, namely five moles for **1**, thirteen moles for **2**, eleven moles for **3**, and eleven moles for **4**. The exothermic second stage is consistent to the loss of dipic molecules, namely two moles for **1**, five moles for **2**, five moles for **3**, and five moles for **4**. The final decomposition products are CoO and NiO for **1**, CoO and NiO for **2**, CuO and NiO for **3**, and CuO and NiO for **4**, and they are identified by IR spectroscopy (Table 2).

The electronic spectra of compounds **1-4** and the free ligand H$_2$dipic were recorded in water and in DMSO solution with 1x10^{-3} molL^{-1} concentrationsat room temperature (Table 3, Figure 2). The characteristic π- π* transitions in the spectrum of **1** are of 280 nm, 285 nm for **2**, 290 nm for **3**, 275 nm for **4** in water, and 289 nm for **1**, 280 nm for **2**, 279 nm for **3**, 269 nm for **4** in DMSO, and with the same profiles as the free ligand H$_2$dipic (286 nm in water/ethanol and 297 nm in DMSO). The bands for the d-d transitions are observed at 750 and 760 nm for **1**, 761 and

767 nm for **2**, 750 and 765 nm for **3**, and 750 and 765 for **4** in water and 770 and 790 nm for **1**, 774 and 795 nm for **2**, 740 and 760 nm for **3**, and 745 and 775 for **4** in DMSO (Table 3).

Table 2. Thermal analyses results of compounds **2-5**.

Compound	Temperature (ºC)	DTG$_{max}$ (ºC)	Leaving group	Found (%)	Calculated (%)
1	30-175	165	5H$_2$O	17.10	16.27
	175-450	205, 276, 350	2dipic	59.00	59.72
	-	-	Co, Ni	23.90	24.01
2	30-200	190	13H$_2$O	17.10	17.09
	200-500	215, 280, 376	5dipic	60.40	60.30
	-	-	Co, Ni	22.50	22.61
3	30-180	165	11H$_2$O	14.90	14.88
	180-550	210, 280, 380	5dipic	62.00	61.99
	-	-	Cu, Ni	23.10	23.13
4	30-155	150	11H$_2$O	14.80	14.88
	185-600	215, 280, 376	5dipic	62.20	61.99
	-	-	Cu, Ni	23.00	23.13

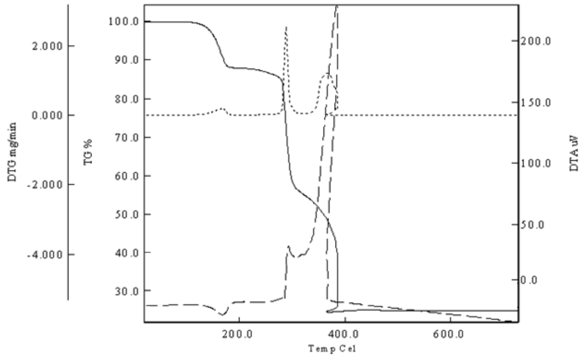

Figure 2. The TG-DTG and DTA curves of **1**.

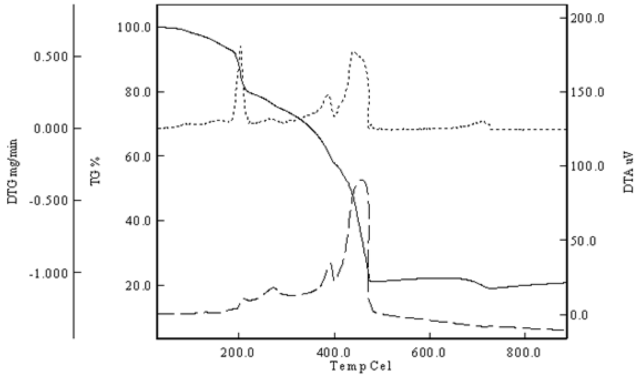

Figure 3. The TG-DTG and DTA curves of **2**.

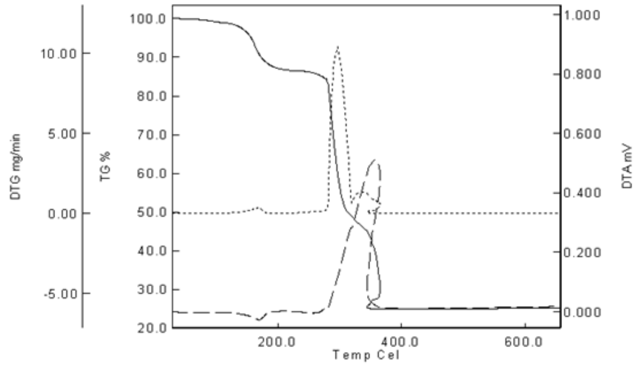

Figure 4. The TG-DTG and DTA curves of **3**.

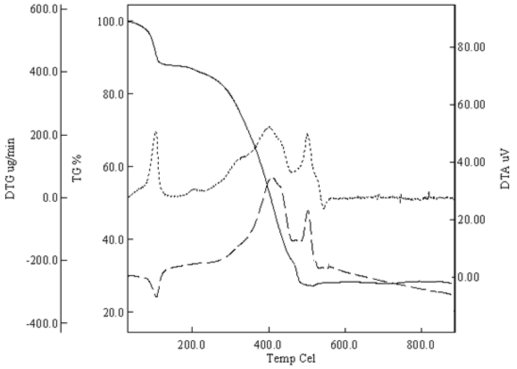

Figure 5. The TG-DTG and DTA curves of **4**.

Table 3. Optical properties for all compounds in water and in DMSO (nm (Lmol^{-1}cm^{-1}).

Compund	**H$_2$dipic**	**1**	**2**	**3**	**4**
Water	286 (19860)	280(32050) 760(300) 750(250)	285(31090) 761(200) 767(140)	290(32050) 765(300) 750(250)	275(31090) 765(200) 750(140)
DMSO	297 (36160)	289(32990) 790(200) 770(150)	280(37380) 795(400) 774(100)	279(32990) 760(200) 740(150)	269(37380) 775(400) 745(100)

The room temperature magnetic moment of the metal complexes is of 5.94 BM for **2**, 3.82 BM for **3**, 2.78 BM for **4**, and 4.85 BM for **5** per metal ion, indicating the presence of five (Fe^{3+}, d^5), three (Co^{2+}, d^7), two (Ni^{2+}, d^8), and four (Fe^{2+}, d^6) unpaired electrons.

The molar conductivity data in water in DMSO are of 6.5 $\Omega^{-1}cm^2mol^{-1}$ for **1**, 9.5 $\Omega^{-1}cm^2$ mol^{-1} for **2**, 5.8 $\Omega^{-1}cm^2$ mol^{-1} for **3**, and 3.2 $\Omega^{-1}cm^2$ mol^{-1} for **4**, indicating that the complexes **1-4** are non-ionic complex [30].

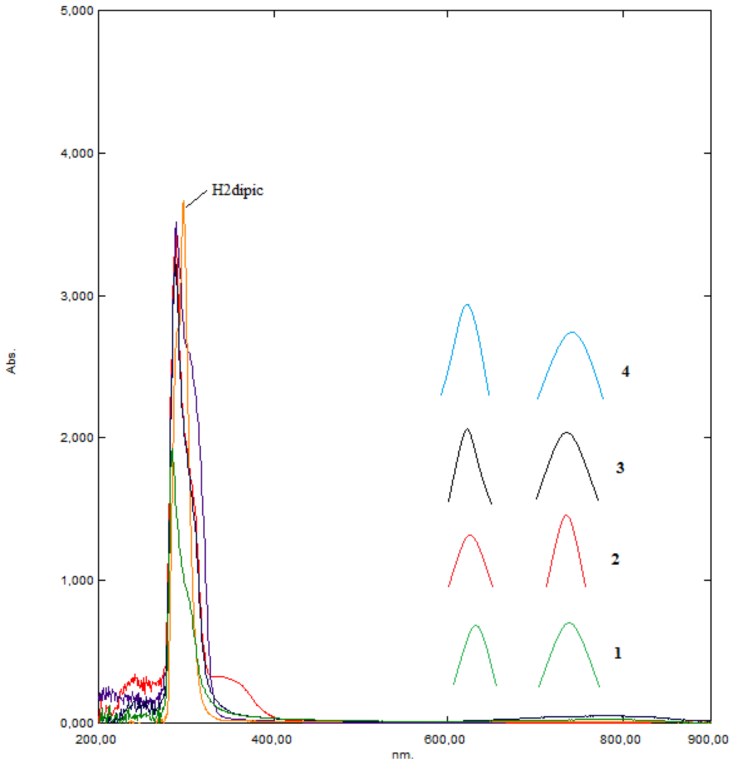

Figure 2. UV–Vis spectra of compounds all compounds in DMSO.

CONCLUSION

In the present work, four newly compounds (**1-4**) were prepared for the first time. The structures of **1-4** might be proposed as octahedral ([Cu(dipic)(H_2O)] unit for **2** square plane) according to results of elemental, spectral, thermal analyses, magnetic measurement and molar conductivity.

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