Macedonian Journal of Chemistry and Chemical Engineering, Vol. **38**, No. 1, pp. 13–17 (2019)

MJCCA9 – 764

ISSN 1857-5552
e-ISSN 1857-5625
DOI: 10.20450/mjcce.2019.1698
Original scientific paper

Received: February 7, 2019
Accepted: March 27, 2019

SYNTHESIS AND CHARACTERIZATION OF MIXED-LIGAND Cu(II) COMPLEXES OF 2-METHOXY-5-SULFAMOYLBENZOIC ACID AND 2-AMINOPYRIDINE DERIVATIVES

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A novel Cu(II) complex **1** of 2-methoxy-5-sulfamoylbenzoic acid (Hsba) and eight novel mixed-ligand Cu(II) complexes **2–9** have been prepared using Hsba and 2-aminopyridine derivatives [2,3-diaminopyridine (2,3dap), 2,3-diamino-5-bromopyridine (2,3da5Brp), 2,3-diamino-5-chloropyridine (2,3da5Clp), 2-amino-3-benzyloxypyridine (2a3bxp), 2-amino-3-hydroxypyridine (2a3OHp), 2-amino-3-methylpiridine (2a3mp), 2-amino-3-methyl-6-ethylpiridine (2a3m6Etp) and 2-amino-3-nitro-6-methylpiridine (2a3$NO_2$6mp)], respectively. The structures of the amorphous metal complexes have been proposed by evaluating the data obtained from elemental analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), Fourier-transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–Vis), magnetic susceptibility and molar conductivity methods.

Keywords: 2-methoxy-5-sulfamoylbenzoic acid; 2-aminopyridine; mixed-ligand; Cu(II) complex

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НА КОМПЛЕКСИ НА Cu(II) СО МЕШАНИ ЛИГАНДНИ НА 2-МЕТОКСИ-5-СУЛФАМОИЛБЕНЗОЕВА КИСЕЛИНА И 2-АМИНОПИРИДИНСКИ ДЕРИВАТИ

Синтетизиран е нов комплекс на Cu(II) **1** на 2-метокси-5-сулфамоилбензоева киселина (Hsba), како и осум нови комплекси на Cu(II) **2–9** со мешани лиганди со употреба на Hsba и соодветни 2-аминопиридински деривати [2,3-диаминопиридин (2,3dap), 2,3-диамино-5-бромопиридин (2,3da5Brp), 2,3-диамино-5-хлоропиридин (2,3da5Clp), 2-амино-3-бензилокси-пиридин (2a3bxp), 2-амино-3-хидроксипиридин (2a3OHp), 2-амино-3-метилпиридин (2a3mp), 2-амино-3-метил-6-етилпиридин (2a3m6Etp) и 2-амино-3-нитро-6-метилпиридин (2a3$NO_2$6mp)]. Предложени се структури на аморфни метални комплекси врз основа на добиените податоци од елементна анализа, индуктивна спрегната плазмена оптичка емисиона спектрометрија (ICP-OES), Фуриеова трансформна инфрацрвена спектроскопија (FTIR), ултравиолетова видлива спектроскопија (UV–Vis), магнетен сусцептибилитет и моларни кондуктометриски методи.

Клучни зборови: 2-метокси-5-сулфамоилбензоева киселина; 2-аминопиридин; мешани лигнади; комплекс на Cu(II)

1. INTRODUCTION

Compounds containing sulfamoyl groups constitute an important class of drugs with several types of pharmacological agents exhibiting anti-glaucoma, anticonvulsant, antioxidant, anticholinesterase, antiinflammatory, antibacterial, protease inhibitor and antitumor activity, among others [1–8]. The simple transition metal complex of 2-methoxy-5-sulfamoylbenzoic acid (Hsba) has not been synthesized and there are few reports on the synthesis and structural characterization of mixed-ligand complexes of sulfamoylbenzoic acid derivatives (furosedime [9], 4-sulfamoylbenzoic acid [10, 11], 2,4-dichloro-5-sulfamoylbenzoic acid [4]) with other ligands (such as *m*-chlorobenzoic acid [9], nicotinamide [10], di-2-pyridylamine [11], 2-aminomethylpyridine [4]).

2-Aminopyridines serve as useful chelating ligands in a variety of inorganic and organometallic applications [12] and also act as monodentate ligands that coordinate metal ions through the aromatic nitrogen in most cases [12–14]. In addition, there are several reports on 2-aminopyridine complexes in which the amino group also participates in coordination [4, 15–17].

The chemistry of copper(II) carboxylate complexes with N-donor ligands, especially with aminopyridine, has been studied extensively over the past few decades [12–17]. Two types of ligands, generally carboxylates and bases (e.g. amines), are brought together before coordination to the metal ion in order to prepare mixed-ligand complexes [12–17].

In this study, a novel Cu(II) complex **1** of 2-methoxy-5-sulfamoylbenzoic acid (Hsba) and eight novel mixed-ligand Cu(II) complexes **2–9** have been prepared using Hsba and 2-aminopyridine derivatives [2,3-diaminopyridine (2,3dap for **2**), 2,3-diamino-5-bromopyridine (2,3da5Brp for **3**), 2,3-diamino-5-chloropyridine (2,3da5Clp for **4**), 2-amino-3-benzyloxypyridine (2a3bxp for **5**), 2-amino-3-hydroxypyridine (2a3OHp for **6**), 2-amino-3-methylpiridine (2a3mp for **7**), 2-amino-3-methyl-6-ethylpiridine (2a3m6Etp for **8**) and 2-amino-3-nitro-6-methylpiridine (2a3NO$_2$6mp for **9**)], respectively. The structures of amorphous metal complexes have been proposed by evaluating the data obtained from elemental analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), Fourier-transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–Vis), magnetic susceptibility and molar conductivity methods.

2. EXPERIMENTAL

2.1. *Materials*

All reagents were the highest grade commercially available and used without further purification. Elemental analyses for C, H, N and S were performed on an Elementar Vario III EL (Hanau, Germany) and Cu was detected using a Perkin Elmer Optima 4300 DV ICP-OES spectrometer (Perkin Elmer, Wellesley, MA). FT-IR spectra were recorded in the 4000–400 cm^{-1} region with a Bruker Optics Vertex 70 FT-IR spectrometer (Ettlingen, Germany) using attenuated total reflection (ATR). UV–Vis spectra were recorded in the 200–900 nm region for aqueous solutions of the compounds (10^{-3} M) using a Shimadzu UV-2550 spectrometer (Shimadzu, Kyoto, Japan). Magnetic susceptibility measurements at room temperature were performed on a Sherwood Scientific Magway MSB MK1 (Sherwood Scientific, Cambridge, UK) magnetic balance using the Gouy method with Hg[Co(SCN)$_4$] as calibrant. Molar conductances of the compounds were determined in water/ethanol (1:1) and DMSO (10^{-3} M) at room temperature using a WTW Cond 315i/SET conductivity meter (Weilheim, Germany).

2.2. *Synthesis of metal complexes* **1–9**

A solution of 1.00 mmol (0.199 g) of $Cu(CH_3COO)_2·H_2O$ in water (10 ml) was added dropwise to a solution of 2.00 mmol (0.462 g) of Hsba for **1** in water/ethanol (1:1, 30 ml) with stirring for five days at room temperature to give a blue amorphous solid for **1** (0.423 g, 65 % yield) (see Fig. 1).

A solution of 1.00 mmol (0.199 g) of $Cu(CH_3COO)_2·H_2O$ in water (10 ml) was added dropwise to a mixed-ligand solution of 2.00 mmol (0.462 g) of Hsba and 2.00 mmol of a 2-aminopyridine derivative (0.218 g of 2,3dap for **2**; 0.376 g of 2,3da5Brp for **3**; 0.287 g of 2,3da5Clp for **4**; 0.400 g of 2a3bxp for **5**; 0.220 g of 2a3OHp for **6**; 0.216 g of 2a3mp for **7**; 0.272 g of 2a3m6Etp for **8**; 0.306 g of 2a3NO$_2$6mp for **9**) in water/ethanol (1:1, 30 ml) with stirring for five days at room temperature to give a green amorphous solid (0.494 g/65 % yield for **2**; 0.624 g/68 % yield for **3**; 0.605 g/73 % yield for **4**; 0.669 g/71 % yield for **5**; 0.534 g/70 % yield for **6**; 0.531 g/70 % yield for **7**; 0.603 g/74 % yield for **8**; 0.646 g/79 % yield for **9**) (see Fig. 1).

Anal. Calcd. for **1** ($C_{16}H_{20}N_2O_{12}S_2Cu$, M_r = 560.01): C, 34.33 %; H, 3.58 %; N, 5.01 %; S, 11.44 %; Cu, 11.30 %. Found: C, 34.32 %; H, 3.60 %; N, 5.00 %; S, 11.45 %; Cu, 11.35 %; for **2** ($C_{26}H_{32}N_8O_{11}S_2Cu$, M_r = 760.26): C, 41.10 %; H, 4.25 %; N, 14.75 %; S, 8.45 %; Cu, 8.35 %. Found: C, 41.08 %; H, 4.24 %; N, 14.74 %; S, 8.44 %; Cu, 8.36 %; for **3** ($C_{26}H_{30}Br_2N_8O_{11}S_2Cu$, M_r = 918.05): C, 34.00 %; H, 3.31 %; N, 12.20 %; S, 7.01 %; Cu, 6.90 %. Found: C, 34.02 %; H, 3.29 %; N, 12.21 %; S, 6.99 %; Cu, 6.92 %; for **4** ($C_{26}H_{30}Cl_2N_8O_{11}S_2Cu$, M_r = 829.15): C, 37.65 %; H, 3.67 %; N, 7.67 %; S, 13.51 %; Cu, 7.75 %. Found: C, 37.66 %; H, 3.65 %; N, 7.66 %; S, 13.51 %; Cu, 7.73 %; for **5** ($C_{40}H_{42}N_6O_{13}S_2Cu$, M_r = 942.47): C, 51.00 %; H, 4.50 %; N, 8.93 %; S, 6.81 %; Cu, 6.77 %. Found:

C, 50.98 %; H, 4.49 %; N, 8.92 %; S, 6.80 %; Cu, 6.74 %; for **6** ($C_{26}H_{30}N_6O_{13}S_2Cu$, M_r = 762.22): C, 41.00 %; H, 3.96 %; N, 11.05 %; S, 8.42 %; Cu, 8.36 %. Found: C, 40.97 %; H, 3.97 %; N, 11.03 %; S, 8.41 %; Cu, 8.34 %; for **7** ($C_{28}H_{34}N_6O_{11}S_2Cu$, M_r = 758.28): C, 44.38 %; H, 4.50 %; N, 11.10 %; S, 8.48 %; Cu, 8.36 %. Found: C, 44.35 %; H, 4.52 %; N, 11.08 %; S, 8.46 %; Cu, 8.38 %; for **8** ($C_{32}H_{42}N_6O_{11}S_2Cu$, M_r = 814.39): C, 47.21 %; H, 5.21 %; N, 10.35 %; S, 7.90 %; Cu, 7.85 %. Found: C, 47.19 %; H, 5.20 %; N, 10.32 %; S, 7.87 %; Cu, 7.80 %; for **9** ($C_{28}H_{30}N_6O_{15}S_2Cu$, M_r = 848.27): C, 41.13 %; H, 3.75 %; N, 10.30 %; S, 7.85 %; Cu, 7.80 %. Found: C, 41.10 %; H, 3.70 %; N, 10.27 %; S, 7.84 %; Cu, 7.77 %.

3. RESULTS AND DISCUSSION

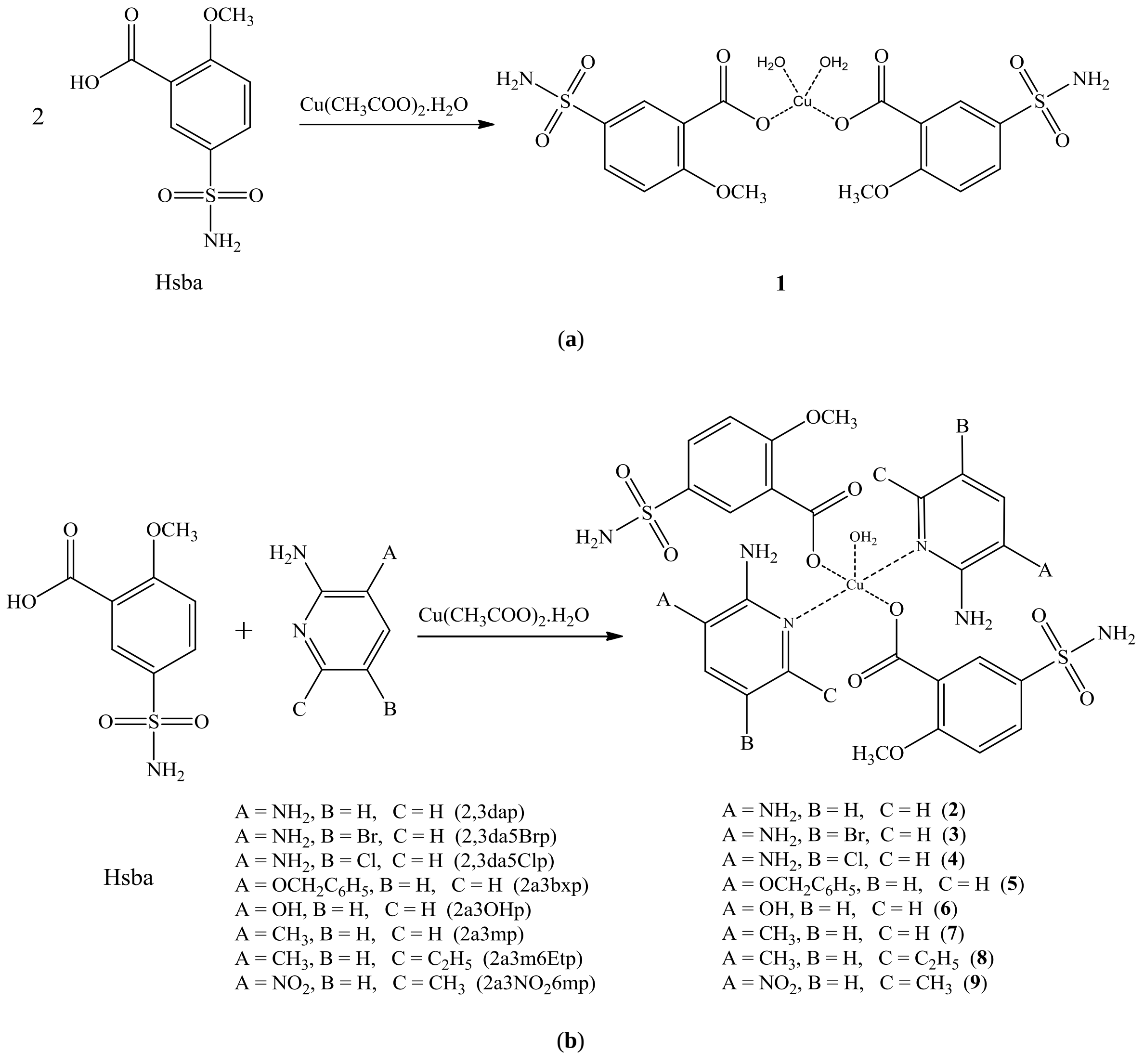
The infrared spectral data of free ligands (Table S1) and compounds **1**–**9** (Table S2 and Figures S1–S9) are given in a supplementary file. In the high frequency region, weak bands at 3110–3052 cm^{-1} and 3034–2727 cm^{-1} are attributed to the stretching vibrations of aromatic (all compounds) and aliphatic C–H (Hsba, 2a3bxp, 2a3mp, 2a3m6Etp, 2a3$NO_2$6mp and **1**–**9**). There are also broad absorption bands at 3582–3427 cm^{-1}, attributed to the ν(OH) vibrations of coordinated water in compounds **1**–**9**, and at 2900 and 3422 cm^{-1}, attributed to the ν(OH) vibrations of the carboxylate group of Hsba and 2a3OHp, respectively. NH_2 vibrations of sulfonamide (Hsba at 3364 and 3289 cm^{-1}) and aminopyridines (3374–3115 cm^{-1}) in **1** (3370 and 3251 cm^{-1}), in **2** (3396, 3372, 3336 and 3188 cm^{-1}), in **3** (3384 and 3205 cm^{-1}), in **4** (3302 and 3217 cm^{-1}), in **5** (3319, 3229, 3280 and 3202 cm^{-1}), in **6** (3372 and 3275 cm^{-1}), in **7** (3476, 3382, 3321 and 3289 cm^{-1}), in **8** (3435, 3371, 3266 and 3186 cm^{-1}) and in **9** (3428, 3292, 3231 and 3154 cm^{-1}) are observed with a similar pattern. Carboxylate groups exhibit strong carbonyl bands at 1700–1456 cm^{-1}. These bands are reflected by FTIR spectra of the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations at 1684 and 1480 cm^{-1} for Hsba, 1612 and 1467 cm^{-1} for **1**, 1626 and 1475 cm^{-1} for **2**, 1621 and 1475 cm^{-1} for **3**, 1621 and 1469 cm^{-1} for **4**, 1626 and 1472 cm^{-1} for **5**, 1612 and 1463 cm^{-1} for **6**, 1623 and 1481 cm^{-1} for **7**, 1639 and 1484 cm^{-1} for **8** and 1636 and 1486 cm^{-1} for **9.** Differences ($\Delta\upsilon$) between the asymmetric and symmetric stretches of the carboxylate groups of **1**–**9** are 145, 151, 146, 152, 154, 149, 142, 155 and 150 cm^{-1}, respectively, which suggests monodentate binding of the carboxylate group to the metal ion in all complexes [18]. Strong absorption bands at 1619–1413 cm^{-1} are attributed to the ν(C=N) and ν(C=C) vibrations for all compounds. The N–O vibration data of the nitro group for 2a3$NO_2$6mp (1531 and 1336 cm^{-1}) and for **9** (1558 and 1335 cm^{-1}) and the C–O vibration data for free ligands, Hsba, 2a3bxp, 2a3OHp and compounds **1**–**9** are between 1387 and 1050 cm^{-1} as expected. Strong absorption bands for SO_2 groups in Hsba and in compounds **1**–**9** are observed at 1331–1121 cm^{-1} with similar profiles and almost similar vibrations. Ring wagging vibrations of the pyridine groups are also observed at 798–750 cm^{-1} for compounds 23dap, 23da5Brp, 23da5Clp, 2a3bxp, 2a3OHp, 2a3mp, 2a3m6Etp, 2a3$NO_2$6mp and **2**–**9**. Weak bands at 496–450 cm^{-1} and 606–559 cm^{-1} are from the M–N (for **2**–**9**) and M–O (for **1**–**9**) vibrations, respectively.

The electronic spectra of compounds **1**–**9** (Figs S10–S18) and the free ligands, Hsba, 2,3dap, 2,3da5Brp, 2,3da5Clp, 2a3bxp, 2a3OHp, 2a3mp, 2a3m6Etp and 2a3$NO_2$6mp were recorded in DMSO solution at $1 \cdot 10^{-3}$ M concentration and room temperature (Table S3). Characteristic π–π^* transitions in the range 269–426 nm (4660–47900 l mol^{-1} cm^{-1}) for all compounds are observed in DMSO. The same π–π^* transition profiles are also detected for the free ligands, Hsba, 2,3dap, 2,3da5Brp, 2,3da5Clp, 2a3bxp, 2a3OHp, 2a3mp, 2a3m6Etp and 2a3$NO_2$6mp, and there is no marked difference from those of metal complexes. Bands for the d–d transitions in DMSO are observed at 786 nm (190 l mol^{-1} cm^{-1}) for **1**, 794 nm (290 l mol^{-1} cm^{-1}) for **2**, 788 nm (260 l mol^{-1} cm^{-1}) for **3**, 773 nm (250 l mol^{-1} cm^{-1}) for **4**, 770 nm (140 l mol^{-1} cm^{-1}) for **5**, 735 nm (260 l mol^{-1} cm^{-1}) for **6**, 771 nm (150 l mol^{-1} cm^{-1}) for **7**, 798 nm (160 l mol^{-1} cm^{-1}) for **8** and 784 nm (180 l mol^{-1} cm^{-1}) for **9**.

The room temperature magnetic moments of the metal complexes are 1.70 μ_B for **1**, 1.65 μ_B for **2**, 1.61 μ_B for **3**, 1.62 μ_B for **4**, 1.68 μ_B for **5**, 1.75 μ_B for **6**, 1.64 μ_B for **7**, 1.65 μ_B for **8** and 1.71 μ_B for **9** per metal ion, indicating the presence of one (d^9) unpaired electron.

The molar conductivity data in DMSO are 2.90 Ω^{-1} cm^2 mol^{-1} for **1**, 2.80 Ω^{-1} cm^2 mol^{-1} for **2**, 2.95 Ω^{-1} cm^2 mol^{-1} for **3**, 3.20 Ω^{-1} cm^2 mol^{-1} for **4**, 4.20 Ω^{-1} cm^2 mol^{-1} for **5**, 2.50 Ω^{-1} cm^2 mol^{-1} for **6**, 4.80 Ω^{-1} cm^2 mol^{-1} for **7**, 4.80 Ω^{-1} cm^2 mol^{-1} for **8** and 3.50 Ω^{-1} cm^2 mol^{-1} for **9**, indicating that all the complexes (**1**–**9**) are non-ionic [19].

The very powerful single-crystal X-ray diffraction method cannot be applied to identify the structures of complexes **1**–**9** due to their powdery form. Formulae for the complexes were proposed using elemental analysis and ICP-OES, with the aid of spectral (FTIR, UV–Vis), magnetic susceptibility and molar conductivity methods (see Fig. 1).



Hsba

1

Hsba

$A = NH_2, B = H, C = H$ (2,3dap)
$A = NH_2, B = Br, C = H$ (2,3da5Brp)
$A = NH_2, B = Cl, C = H$ (2,3da5Clp)
$A = OCH_2C_6H_5, B = H, C = H$ (2a3bxp)
$A = OH, B = H, C = H$ (2a3OHp)
$A = CH_3, B = H, C = H$ (2a3mp)
$A = CH_3, B = H, C = C_2H_5$ (2a3m6Etp)
$A = NO_2, B = H, C = CH_3$ (2a3NO26mp)

$A = NH_2, B = H, C = H$ (**2**)
$A = NH_2, B = Br, C = H$ (**3**)
$A = NH_2, B = Cl, C = H$ (**4**)
$A = OCH_2C_6H_5, B = H, C = H$ (**5**)
$A = OH, B = H, C = H$ (**6**)
$A = CH_3, B = H, C = H$ (**7**)
$A = CH_3, B = H, C = C_2H_5$ (**8**)
$A = NO_2, B = H, C = CH_3$ (**9**)

Fig. 1. Syntheses of compounds: (**a**) complex **1;** (**b**) complexes **2–9**

4. CONCLUSIONS

In this present work, a novel Cu(II) complex **1** of Hsba and eight novel mixed-ligand Cu(II) complexes **2–9** have been prepared from Hsba and 2-aminopyridine derivatives, respectively. The formulae for complexes **1–9** have been proposed using the results from elemental analysis, spectral, magnetic measurement and molar conductivity methods.

Acknowledgments. The authors acknowledge the support provided by Kutahya Dumlupınar University Research Fund (Grant No. 2016/89).

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