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Nickel(II) and copper(II) complexes with an asymmetric bidentate Schiff-base ligand derived from furfurylamine

Synthesis, spectral, XRD, and thermal studies

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Abstract New asymmetric bidentate Schiff-base ligand (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine, (HL), and its nickel(II) and copper(II) complexes with the general composition ML_2 [M = Ni (**1**) and Cu (**2**)], were prepared. The ligand and the metal complexes were characterized by elemental analysis, FT-IR, and UV–Vis spectroscopy. In addition, ^{1}H-NMR and X-ray powder diffraction (XRD) were employed for characterization of ligand and metal complexes, respectively. Thermogravimetric analysis (TGA) of the ligand and metal complexes revealed the thermal stability and decomposition pattern of the species.

Keywords Schiff-base · Nickel(II) · Copper(II) · Spectroscopy · Thermogravimetry

Introduction

A large number of nickel(II) and copper(II) complexes with salicylaldehyde Schiff-base ligands have been extensively studied for their interesting structural [1–7] application and properties [8–14]. Asymmetric Schiff-base ligands have many advantages over their symmetrical counterparts in the composition and geometry of transition metal complexes and properties [15–18]. The thermal decomposition of the complexes of Ni(II) and Cu(II) with Schiff-base ligands have been extensively studied in recent years [19–27]. However, reports on the synthesis of transition metal complexes with Schiff-base derived from furfurylamine have been very scarce [28, 29]. In this article, an asymmetric bidentate Schiff-base ligand (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine, (HL), and their nickel(II) and copper(II) complexes with the general composition ML_2 [M = Ni (**1**) and Cu (**2**)] were prepared and characterized (Fig. 1).

Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. Infrared spectra were recorded using KBr disks on a FT-IR Perkin-Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. TheTGAs were performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20 °C/min from 35–700 °C. X-ray diffraction (XRD) patterns of the complexes were recorded on a Bruker AXS diffractometer D8 ADVANCE, with Cu-K_α radiation filtered by a nickel monochromator and operated at 40 kV and 30 mA. Diffraction patterns were recorded in the range $2\theta = 10^\circ$–70°. UV–Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer; $\lambda_{max}/\varepsilon$ in nm.

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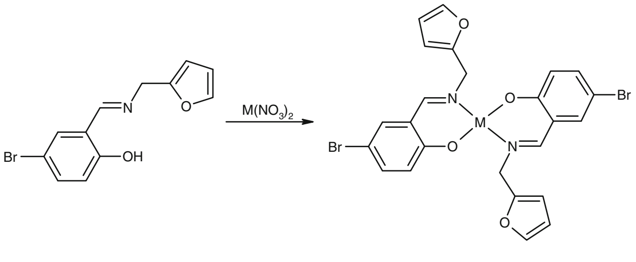

M = Ni (1) and Cu (2)

Fig. 1 Chemical structures of the Schiff-base ligand (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine, (HL), and its nickel(II) and copper(II) complexes

Preparation of (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine, (HL)

2-Furfurylamine (0.97 g, 10 mmol) in methanol (10 mL) and a methanolic solution (20 mL) of an equimolar amount of 5-bromosalisylaldehyde (1.9 g, 10 mmol) were mixed; the mixed solution immediately turned yellow. After stirring at 50 °C for 1 h, the solvent was removed by rotary evaporation to obtain yellow precipitations. Crystallization from a mixture of chloroform–methanol (1:1 v/v, 20 mL) gave the pure products as yellow crystalline compounds (yield: 86%).

Preparation of complexes

Methanolic solutions (20 mL) of $Ni(NO_3)_2.6H_2O$ (**1**) and $Cu(NO_3)_2 \cdot 3H_2O$ (**2**) taken from two separate reactors in molar ratio of 2:1 were mixed with a methanolic solution (20 mL) of (5-bromo-2-hydroxybenzyl-2-furylmethyl) imine (0.56 g, 2 mmol). After stirring for 1 h at 323 K, the solutions were left to cool overnight at room temperature. The microcrystalline products of complexes were filtered off, washed with cold methanol, and dried at room temperature for several days.

Results and discussion

The 2-Furfurylamine and 5-bromosalisylaldehyde used for preparation of ligand was from Merck Chemical Company. The metal salts used were in the hydrated form, i.e., $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ and were purchased from Merck Chemical Company. The organic solvents are reagent grade chemicals and used as received. The Schiff-base ligand is soluble in all common solvents such as acetone, methanol, chloroform, etc., but complexes are soluble in coordinated solvents such as DMF, DMSO, and CH_3CN, partly soluble in methanol and ethanol, and completely insoluble in acetone, dichloromethane, and chloroform. Elemental analyses are shown in Table 1. The analytic data show that the complexes may be formulated as ML_2, where L = (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine and M = Ni (**1**) and Cu (**2**).

Table 1 Analytic data for ligand and its Ni(II) and Cu(II) complexes

Compound	Found/calc./%		
	C	H	N
Ligand HL	51.54/51.45	3.26/3.59	4.97/5.00
NiL_2 (**1**)	45.99/46.36	2.64/2.92	4.45/4.50
CuL_2 (**2**)	46.54/46.72	2.75/2.94	4.54/4.54

Table 2 Selected FT-IR data for ligand and its Ni(II) and Cu(II) complexes (cm^{-1})

Compound	υ (C=N)	υ (–CH=N)	υ (C–O)	υ (C–N)
Ligand HL	1633	2902	1282	1384
NiL_2 (**1**)	1615	2935	1332	1423
CuL_2 (**2**)	1623	2922	1327	1421

Table 3 Electronic data of ligand and complexes **1** and **2**

Compound	Solvent	λ_{max}/nm/ε/$M^{-1}cm^{-1}$
Ligand HL	Chloroform	242/108610, 252/101120, 331/40618
NiL_2 (**1**)	DMSO	250/56525, 335/11869, 428/5982, 625/121
CuL_2 (**2**)	DMSO	244/59574, 304/12408, 382/11777, 615/140

Infrared spectra

The assignment of the significant FT-IR spectral bands of ligand and its Ni(II) and Cu(II) complexes are presented in Table 2. The FT-IR spectra of the Ni(II) and Cu(II) complexes were compared with HL ligand to get some information about binding the ligand to nickel and copper in the complexes. The FT-IR spectrum of ligand exhibits a strong band of the azomethine (C=N) at 1633 cm^{-1} [28, 29]. This band is shifted to the 1615 cm^{-1} in **1** and 1623 cm^{-1} in **2**, confirming the azomethine–metal coordination as was expected [28, 29]. The spectra of free ligand shows strong band in 1282 and 1384 cm^{-1}, assigned to the C–O and C–N stretching of the ligand. However, after complexation of C–O and C–N groups via oxygen and nitrogen to the metal ions, these bands were observed at the regions of 1332 and 1423 cm^{-1} for **1**, and 1327 and 1421 cm^{-1} for **2**.

Electronic spectra

The electronic spectra of ligand and complexes are measured in chloroform and DMSO, respectively, and are presented in Table 3. Ligand and complexes exhibit similar UV spectra. In the UV spectrum of ligand, two anterior peaks are at 242 and 252 nm, attributed to the π–π^* transitions of phenyl ring, and a peak attributed to the C=N group transition is observed at 331 nm [28]. The absorptions in **1** and **2** are all red-shift and broader than in ligand [28]. In the UV–Vis spectrum of complexes, only one d–d transition is observed in the visible region, viz., 625 nm in **1** and 615 nm in **2**.

Thermal behavior of ligand and complexes

The TGAs of ligand and complexes under N_2 were examined. The TG graphs, at a heating rate of 20 K min^{-1}, of the ligand and complexes are represented in Fig. 2a–c. The decomposition stages, temperature range, as well as the found and calculated mass loss percentages of the all compounds are illustrated in Table 4.

The title compounds—ligand, NiL_2 (**1**), and CuL_2 (**2**)—are stable up to 313, 318, and 308 K, respectively, and during further heating undergo decomposition in three stages. In the first stage, ligand shows a mass loss of 7.20% in the temperature range 313–452 K, complex **1** shows a mass loss of 5.23% in the temperature range 318–561 K, and complex **2** shows a mass loss of 7.12% in the temperature range 308–531 K, due to partial decomposition, corresponding to the elimination of one hydroxy group (calcd. 5.19%) in ligand, two hydroxy groups (calcd. 5.50%) in complex **1,** and two hydroxy groups and half oxygen (calcd. 7.27%) in complex **2**.

The second and third decomposition stages of the ligand and complexes are different. In the second stage, ligand shows a mass loss of 88.28% in the temperature range 452–541 K, corresponding to the major stage of the decomposition, i.e., elimination of $C_{12}H_9NBr$ group (calcd. 88.22%), While the third decomposition stage of the ligand is partial and shows a mass loss of 5.72% in the temperature range 541–973 K (one oxygen, calcd. 5.71%).

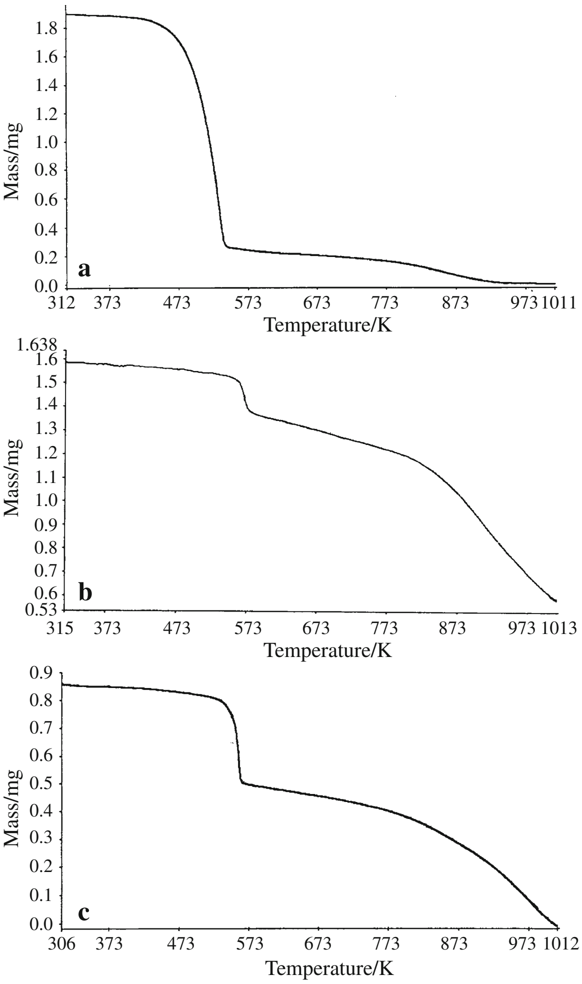

Fig. 2 The TG graphs of the ligand (**a**) **1**, (**b**), and **2** (**c**)

In the second stage, complex **1** shows a mass loss of 7.62% in the temperature range 561–576 K, corresponding to the partial decomposition of **1** and elimination of half Br and half oxygen (calcd. 7.75%), while complex **2** shows a mass loss of 34.66% in the temperature range 531–565 K, corresponding mainly to the decomposition of **2** and elimination of two Br and one $C_4H_3O_{0.5}$ group (calcd. 45.29%).

Table 4 Thermal analysis data of the ligand and complexes **1** and **2**

Compounds	Temperature range/K	Mass loss/%		Products	Residue
		Exp.	Calcd.		
Ligand HL	313–452	7.20	5.19	1 OH	$C_{12}H_9NBrO$
	452–541	85.02	88.22	$C_{12}H_9NBr$	O
	541–973	7.78	5.72	1 O	–
NiL_2 (**1**)	318–561	5.23	5.50	2 OH	$C_{24}H_{18}N_2Br_2O_2Ni$
	561–576	7.62	7.75	0.5 Br + 0.5 O	$C_{24}H_{18}N_2Br_{1.5}O_{1.5}Ni$
	576–973	48.63	45.44	$C_{17}H_{15}NBr_{0.5}O_{0.5}$	$C_7H_3NBrONi$ (41.32%)
CuL_2 (**2**)	308–531	7.12	7.27	2 OH + 0.5 O	$C_{24}H_{18}N_2Br_2O_{1.5}Cu$
	531–565	34.66	35.09	2 Br + $C_4H_3O_{0.5}$	$C_{20}H_{15}N_2OCu$
	565–973	45.32	45.42	$C_{20}H_{15}N_2$	CuO (12.75%)

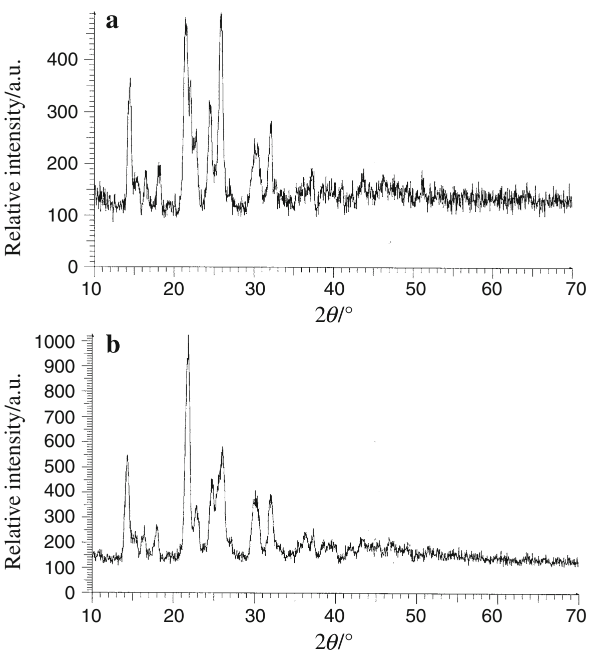

Fig. 3 X-ray powder diffraction patterns of **1** (**a**) and **2** (**b**)

The third decomposition stage of **1** is mainly one of decomposition and shows a mass loss of 48.63% in the temperature range 565–973 K, corresponding to the elimination of one $C_{17}H_{15}NBr_{0.5}O_{0.5}$ group (calcd. 45.44%), while complex **2** shows a mass loss of 45.32% in the temperature range 565–973 K, corresponding to the elimination of one $C_{20}H_{15}N_2$ group (calcd. 45.42%).

Figure 3 shows an X-ray powder diffraction patterns of Ni(II) and Cu(II) complexes. The XRD patterns for complexes are quite the same and suggest that the complexes have similar structure. The structures of the complexes have not been determined because single crystals have not been obtained.

Conclusions

New Schiff-base ligand (5-bromo-2-hydroxybenzyl-2-furylmethyl)imine and its nickel(II) and copper(II) complexes were obtained. The structural properties of ligand and complexes were proposed based on elemental analyses: FT-IR, UV–Vis, ^{1}H-NMR spectroscopy, and thermal analysis. From the FT-IR spectra, it was concluded that the ligand is an anionic bidentate NO chelating and is coordinated to the metal ions through the one azomethine nitrogen atom and one phenolic oxygen atom. However, the complexes have similar structure, but they have dissimilar stages of decomposition.

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