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Spectral, thermal and magnetic properties of Cu(II) and Ni(II) complexes with Schiff base ligands

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Abstract: Mononuclear copper(II) and nickel(II) complexes of the formulae [Cu(L¹)] (**1**), [Ni(L¹)] (**2**), [Cu(L²)] (**3**) and [Cu(L³)H₂O] (**4**) (where L¹ = *N,N'*-ethylenebis(4,6-dimethoxysalicylideneaminato), L² = *N,N'*-ethylenebis(5-bromosalicylideneaminato) and L³ = *N,N'*-ethylenebis(5-bromo-3-methoxysalicylideneaminato)) were synthesized as microcrystalline powders and characterized by IR spectroscopy, thermal analysis and magnetic measurements. The magnetic susceptibility of the Cu(II) complexes changed with temperature according to the Curie–Weiss law. The complexes **1**, **3** and **4** exhibit magnetic moments of 2.29, 2.20 and 1.88 μ_B, respectively, at 303 K. These values practically do not change with lowering the temperature to 77 K. The nickel(II) complex **2** is diamagnetic.

Keywords: copper(II) complexes; Schiff base; magnetic properties.

INTRODUCTION

The interest in the synthesis and characterization of transition metal complexes containing Schiff bases lies in their biological and catalytic activity in many reactions. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural lability and are sensitive to the molecular environment. The environment around the metal center, such as coordination geometry, number of coordinated ligands and their donor group, is a key factor for a metalloprotein to perform specific physiological functions.^{1–10} Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor, enhancing solubility and either performing homogenous or heterogeneous catalyses. Salicylaldimine metal complexes constitute a family of one of the most important systems due to the number of applications in catalysis and biomimetic chemistry. These compounds can be used as

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components for the assembly of supramolecular architectures, displaying interesting structures and properties.^{11–14}

N,N'-Ethylenebis(4,6-dimethoxysalicylideneiminato)copper(II) (**1**), *N,N'*-ethylenebis(4,6-dimethoxysalicylideneaminato)nickel(II) (**2**), *N,N'*-ethylenebis(5-bromosalicylideneaminato)copper(II) (**3**) and aqua(*N,N'*-ethylenebis(5-bromo-3-methoxysalicylideneaminato)copper(II) (**4**) have hitherto not been obtained in powder form. However in the literature there are papers only about their synthesis and crystal structure determination,^{15–18} but there is no the information on their various properties. Therefore, the aim of this work was to obtain complexes of Cu(II) and Ni(II) with the Schiff base ligands as microcrystalline powder and to examine some of their physicochemical properties, including thermal stability in air during heating to 973 K, IR spectral characterization and magnetic behavior in the temperature range of 76–303 K.

EXPERIMENTAL

Materials

All chemicals and solvents used for the syntheses were of commercially available reagent grade and were used without further purification.

Synthesis of the Schiff bases

All the Schiff base ligands ($H_2L^1 = C_{20}H_{24}N_2O_6$, $H_2L^2 = C_{16}H_{14}Br_2N_2O_2$, $H_2L^3 = C_{18}H_{18}Br_2N_2O_4$) were prepared by known methods^{19–21} by the 2:1 condensation of 4,6-dimethoxysalicylaldehyde, 5-bromosalicylaldehyde or 5-bromo-3-methoxysalicylaldehyde, respectively, and ethylenediamine in methanol. The Schiff bases were separated as yellow needles and were recrystallized twice from methanol. The compounds were stable at room temperature and were characterized by IR spectroscopy and elemental analysis. Anal. Calcd. for $C_{20}H_{24}N_2O_6$ (H_2L^1): C, 61.86; H, 6.19; N, 7.22 %. Found: C, 61.80; H, 6.10; N, 7.12 %. Anal. Calcd. for $C_{16}H_{14}Br_2N_2O_2$ (H_2L^2): C, 45.07; H, 3.29; N, 6.57 %. Found: C, 45.12; H, 3.10; N, 6.45 %. Anal. Calcd. for $C_{18}H_{18}Br_2N_2O_4$ (H_2L^3): C, 44.46; H, 3.71; N, 5.76 %. Found: C, 44.36; H, 3.61; N, 5.69 %.

Synthesis of the complexes

Complexes **1**, **3** and **4** were obtained by the treatment of copper(II) nitrate trihydrate (1.0 mmol) with H_2L^1 , H_2L^2 and H_2L^3 (1.0 mmol), respectively in methanolic solution under reflux. For preparation of the complex **2**, nickel(II) nitrate hexahydrate and H_2L^1 were used. The reaction mixtures were cooled and the resulting precipitates were filtered off, washed with diethyl ether and dried.

Methods and apparatus applied

The contents of carbon, hydrogen and nitrogen in the analyzed compounds were determined by elemental analysis using a CHN 2400 Perkin Elmer analyzer.

The contents of copper and nickel were established using an ED-XRF spectrophotometer (Canberra-Packard).

Single-crystal diffraction data for compounds **1–4** were measured at room temperature in the ω mode on a Oxford Diffraction Xcalibur CCD diffractometer using graphite-monochromated MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$).

The infrared spectra of the complexes were recorded in the range of 4000–400 cm^{-1} using an M-80 spectrophotometer (Carl Zeiss, Jena, Germany). Samples for IR spectroscopy measurements were prepared as KBr discs.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 (Setaram) TG/DTA/DSC instrument. The experiments were performed under a dynamic air atmosphere (flow rate 17 mL min^{-1}) in the temperature range of 297–973 K at a heating rate of 5 K min^{-1} . The initial mass of the samples (mg) used for the measurements were following: **1** – 7.33; **2** – 7.24; **3** – 7.44; **4** – 7.25. The samples were heated in Al_2O_3 crucibles.

The X-ray diffraction patterns of the final product of thermal decomposition were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The measurements were performed in the 2θ range 4–80° by means of the Bragg–Brentano method.

The magnetic susceptibility values of the compounds were determined by the Gouy method in the temperature range of 76–303 K. The calibrant employed was $\text{Hg}[\text{Co}(\text{SCN})_4]$ for which a magnetic susceptibility of $1.644 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$ was taken. Correction for diamagnetism of the constituent atoms was calculated using Pascal's constants.²² The effective magnetic moment values, μ_{eff} , were calculated from the equation:

$$\mu_{\text{eff}} = 2.83 (\chi_{\text{M}}T)^{1/2}$$

where χ_{M} is the magnetic susceptibility and T is the absolute temperature.

RESULTS AND DISCUSSION

The elemental analyses (C, H, N and M) data and the IR spectra analysis of the Schiff base complexes, (Tables I and II, respectively) showed that they may be represented by the formulae $[\text{CuC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (**1**), $[\text{NiC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (**2**), $[\text{CuC}_{16}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2]$ (**3**) and $[\text{Cu}(\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_4)\text{H}_2\text{O}]$ (**4**). The structures of **1–4** were also confirmed by single crystal X-ray diffraction. The unit cell parameters of **1** ($P2_1/c$, $a = 7.5548(2) \text{ \AA}$, $b = 15.8484(4) \text{ \AA}$, $c = 15.7716(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.013(3)^\circ$, $\gamma = 90^\circ$ and $V = 1888.1(1) \text{ \AA}^3$) and **2** ($P2_1/c$, $a = 7.5342(3) \text{ \AA}$, $b = 15.7566(5) \text{ \AA}$, $c = 15.8626(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.187(4)^\circ$, $\gamma = 90^\circ$ and $V = 1882.7(1) \text{ \AA}^3$) are similar to those reported earlier by Assey *et al.*^{15,16} Compound **1** is isostructural with **2**.^{15,16} In addition, the unit cell parameters of **3** ($P-1$, $a = 8.3372(9) \text{ \AA}$, $b = 9.6880(11) \text{ \AA}$, $c = 11.0308(12) \text{ \AA}$, $\alpha = 115.259(11)^\circ$, $\beta = 92.689(9)^\circ$, $\gamma = 101.732(9)^\circ$ and $V = 779.9(2) \text{ \AA}^3$) resemble those described by

TABLE I. Elemental analysis data of the Schiff base complexes

Complex	Color	Calcd. (Found), %			
		C	H	N	M
$[\text{CuC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (1)	Brown	53.39	4.89	6.23	14.14
		(53.29)	(4.62)	(6.10)	(13.94)
$[\text{NiC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (2)	Green	53.98	4.95	5.40	13.20
		(53.65)	(4.72)	(5.11)	(13.00)
$[\text{CuC}_{16}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2]$ (3)	Brown	39.40	2.46	5.75	13.04
		(39.14)	(2.17)	(5.44)	(12.76)
$[\text{Cu}(\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_4)\text{H}_2\text{O}]$ (4)	Green	38.21	3.18	4.95	11.24
		(38.04)	(3.04)	(4.82)	(11.12)

Xie *et al.*¹⁷ The unit cell parameters of **4** (*Pnma*, $a = 8.7379(3)$ Å, $b = 27.9612(9)$ Å, $c = 7.9779(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$ and $V = 1949.2(1)$ Å³) are similar to those reported by Xie.¹⁸ These metal complexes are soluble in polar organic solvents, such as MeOH, CHCl₃, DMF and EtOH, but less soluble in non-polar solvents, such as hexane, heptane and toluene.

TABLE II. IR spectral data of the Schiff base ligands and their metal complexes (cm⁻¹)

Compound		$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
C ₂₀ H ₂₄ N ₂ O ₆	H ₂ L ¹	3424	1624	1276	–	–
C ₁₆ H ₁₄ Br ₂ N ₂ O ₂	H ₂ L ²	3416	1636	1216	–	–
C ₁₈ H ₁₈ Br ₂ N ₂ O ₄	H ₂ L ³	3440	1628	1252	–	–
[CuC ₂₀ H ₂₂ N ₂ O ₆]	1	–	1608	1232	555	400
[NiC ₂₀ H ₂₂ N ₂ O ₆]	2	–	1604	1236	548	436
[CuC ₁₆ H ₁₂ Br ₂ N ₂ O ₂]	3	–	1632	1176	544	448
[Cu(C ₁₈ H ₁₆ Br ₂ N ₂ O ₄)H ₂ O]	4	3448	1624	1240	564	464

Infrared spectra

The infrared spectra of the free Schiff base ligands H₂L¹, H₂L² and H₂L³ (Table II) showed a strong band in the region of 1624–1636 cm⁻¹ which is characteristic of the azomethine (C=N) group. In addition to this characteristic (C=N) absorption, these ligands also exhibit broad medium bands with a maximum around 3440 cm⁻¹, which can be assigned to phenolic (O–H) group vibrations. According to the literature,^{23–30} the participation of the nitrogen atom of the Schiff base ligands in the coordination sphere should reduce the bond order in the C=N group due to the strong donation of electron density toward the metal ion, and result in a decrease in the C=N stretching frequency. In the IR spectra of the Schiff base complexes (Table II), the band due to $\nu(\text{C=N})$ showed a negative shift and appeared at 1632–1604 cm⁻¹, indicating coordination of the azomethine nitrogen to copper and nickel metals, respectively.^{8,9,23–30} A strong band observed at 1216–1276 cm⁻¹ in the free Schiff bases is assigned to the phenolic C–O stretching vibration. On complexation, this band is shifted to the lower frequency range of 1240–1176 cm⁻¹, indicating coordination through the phenolic oxygen.^{9,29} This was further supported by the disappearance of the broad $\nu(\text{OH})$ band around 3400 cm⁻¹ in the complexes, indicating deprotonation of the phenolic proton prior to coordination. That the azomethine nitrogen and the phenolic oxygen are involved in complexation with the metal ion is also clearly evident from the appearance of the new medium intensity bands at 548–564 and 400–460 cm⁻¹ in the spectra, assignable to $\nu(\text{M-N})$ and $\nu(\text{M-O})$.^{9,30–32} The bands at 3440 and 3448 cm⁻¹ in the spectra of the H₂L³ ligand and analyzed complex **4**, respectively, have a similar position but their shapes are different. In the spectra of **4**, this intense broad absorption band confirms the presence of water molecules.³⁰

Thermal analysis

The thermal properties of complexes **1–4** were investigated by thermogravimetric (TG) analysis, differential thermogravimetric (DTG) analysis and differential thermal analysis (DTA). The recorded TG/DTG and DTA curves of three copper(II) Schiff base complexes in an air atmosphere are presented in Figs. 1–3. It can be seen that the TG curves of **1** (Fig. 1) and **3** (Fig. 2) show no mass loss up to 573 and 563 K, respectively, indicating the absence of water molecules and other adsorbed solvent molecules in the coordination sphere. As the temperature

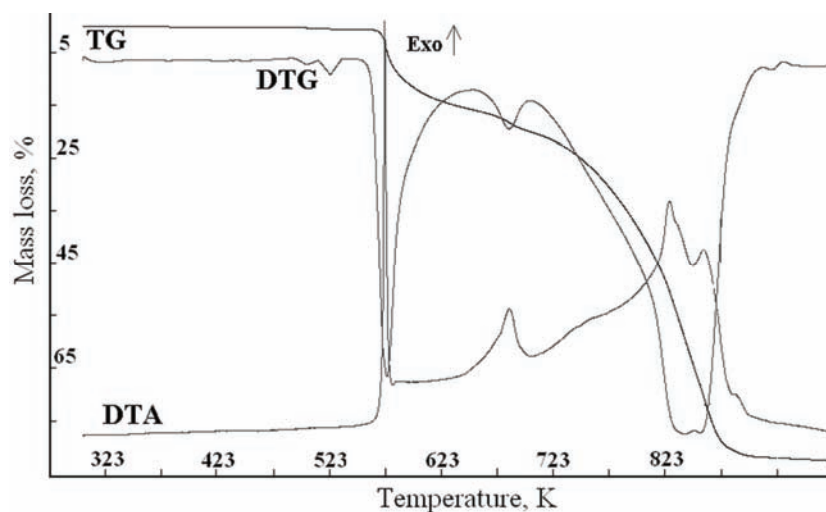


Fig. 1. TG, DTG and DTA curves of $[\text{CuC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (**1**).

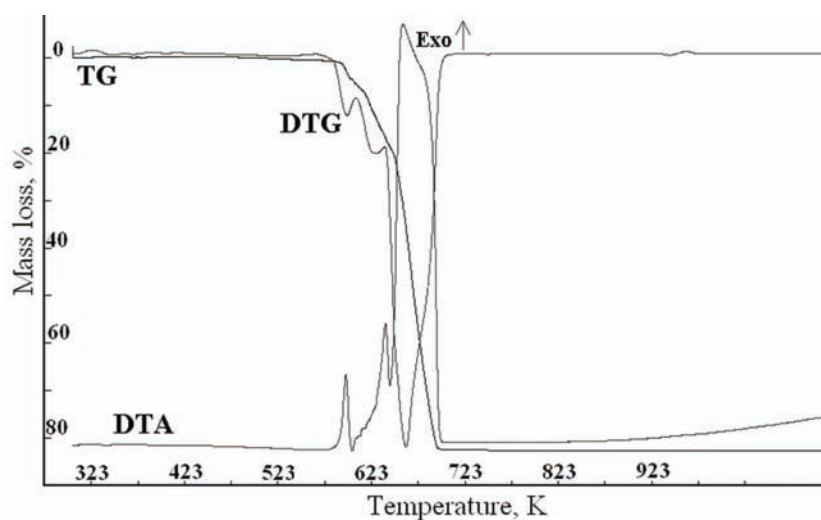


Fig. 2. TG, DTG and DTA curves of $[\text{CuC}_{16}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2]$ (**3**).

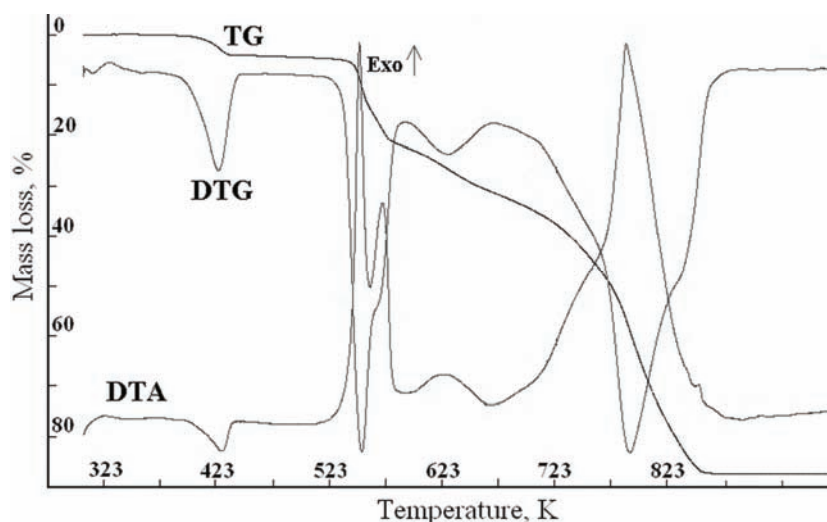


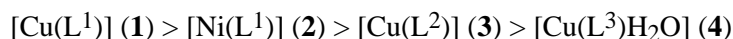
Fig. 3. TG, DTG and DTA curves of $[\text{Cu}(\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_4)\text{H}_2\text{O}]$ (**4**).

was increased, the TG/DTG curves of the copper(II) complexes exhibit a sharp mass loss in the temperature ranges of 578–703 K (**1**) and 563–948 K (**3**), which are accompanied with sharp exothermic peaks in the DTA curves at 656 (**1**), 573 (**3**) and 825 K (**3**) that may be due to the decomposition of the ligand molecule. The complex **2** (nickel (II)) similar to **1**, displays a one-step decomposition. This step shows drastic mass loss within a wide temperature range of 573–713 K with a DTG peak at 673 K, also giving rise to a sharp exothermic peak at 678 K in the DTA curve. This process can be interpreted as decomposition of the ligand molecules. The thermal decomposition of complex **4** occurred in two steps (Fig. 3), giving one endothermic and two exothermic DTA peaks. The first step displays a gradual mass loss of 3.90 % within the temperature range of 413–433 K with a DTG peak at 423 K, which may be attributed to the loss of the one water molecule (calcd. 3.20 %). The recorded DTA curve reveals an endothermic peak at 426 K. The water elimination process occurs at a high temperature. This may indicate the coordination of the water molecules.²³ The anhydrous complex is stable up to 536 K. The next decomposition steps of **4** also exhibit a gradual loss of mass within the temperature range of 536–858 K with DTG peaks at 505 and 788 K. They are probably connected with the decomposition of the Schiff base ligand. Combustion of the organic ligand is accompanied by strong exo-effect peaks seen on the DTA curves with maximums at 547 and 783 K.

The complexes decompose to the respective oxides: CuO (in the case of **1**, **3**, and **4**) and NiO (in the case of **2**).³² The mass losses calculated from the TG curves are in the range of 87.20–82.50 % (the theoretical values are 86.00–82.30

%). The compositions of the final products were calculated from the TG curves and experimentally verified by their X-ray diffraction patterns and IR spectra.

According to the beginning temperature of the decomposition of the Schiff base complexes, the following order of thermal stability may be proposed:



Magnetic properties

The magnetic behavior of the title compounds was studied in the temperature range 77–300 K (Table III). The magnetic susceptibility of the Cu(II) complexes changed with temperature according to the Curie–Weiss law. The magnetic properties of **1** in the form of an χ_M vs. T plot (χ_M is the molar magnetic susceptibility) is shown in Fig. 4. The observed effective moment of complexes **1** and **3** (having square-planar geometry^{15,17}) at 76 K is 2.12 μ_B , while that at room temperature is 2.20 μ_B . The copper(II) ion ($3d^9$) has one unpaired electron in the 3d shell, therefore its compounds were considered to have magnetic moments close to the spin-only value, 1.73 μ_B but due to spin orbit coupling, higher values are often observed.^{29,33–35} The magnetic moment values calculated for **4** are in the range of 1.85–1.88 μ_B . The environment around the copper in **4** is square-pyramidal.¹⁸ The magnetic moments of the copper(II) complexes were treated by

TABLE III. The magnetic data of the Cu(II) complexes with Schiff bases

T / K	[Cu(C ₂₀ H ₂₂ N ₂ O ₆)] (1)		[Cu(C ₁₆ H ₁₂ Br ₂ N ₂ O ₂)] (3)		[Cu(C ₁₈ H ₁₆ Br ₂ N ₂ O ₄)(H ₂ O)] (4)	
	$\chi_M \times 10^6$ cm ³ ·mol ⁻¹	μ_{eff} μ_B	$\chi_M \times 10^6$ cm ³ ·mol ⁻¹	μ_{eff} μ_B	$\chi_M \times 10^6$ cm ³ ·mol ⁻¹	μ_{eff} μ_B
76	7697	2.16	7353	2.12	426166	1.85
123	4475	2.10	4622	2.13	411570	1.82
133	4088	2.09	4236	2.12	412301	1.82
143	3851	2.10	3904	2.11	410964	1.81
153	3501	2.07	3636	2.11	415280	1.82
163	3464	2.13	3422	2.11	412067	1.82
173	3289	2.13	3208	2.11	416636	1.83
183	3152	2.15	3026	2.11	416376	1.83
193	3039	2.17	2897	2.12	421158	1.84
203	2927	2.18	2758	2.12	420026	1.83
213	2840	2.20	2597	2.10	419467	1.83
223	2740	2.21	2426	2.08	422846	1.84
233	2640	2.22	2351	2.09	423211	1.84
243	2552	2.23	2287	2.11	426829	1.85
253	2465	2.23	2169	2.10	429249	1.85
263	2402	2.25	2201	2.15	430473	1.86
273	2402	2.27	2083	2.11	429744	1.86
283	2278	2.27	2040	2.13	433092	1.86
293	2253	2.30	1944	2.12	436703	1.87
303	2165	2.29	1987	2.20	441532	1.88

Boudreaux. According to Boudreaux, in complexes having a square pyramidal configuration, the five-fold degenerate 3d level of Cu(II) is split by a ligand field of C_{4v} symmetry into four components. The $d_{x^2-y^2}$, d_{x^2} and d_{xy} levels are non degenerate, while (d_{xz} , d_{yz}) levels are four-fold degenerate, including spin. The spin-orbit interaction splits this level into two components, each of which is further split into two sublevels by the external magnetic field. Boudreaux calculated theoretically the magnetic moment of square-pyramidal copper(II) complexes to be 2.11–2.21 μ_B at room temperature.^{36,37} These values are slightly higher than those obtained during the experimental measurements (1.88 μ_B). The nickel(II) complex **2** (having a square planar geometry ¹⁶) is diamagnetic.^{2,4,23,33,38}

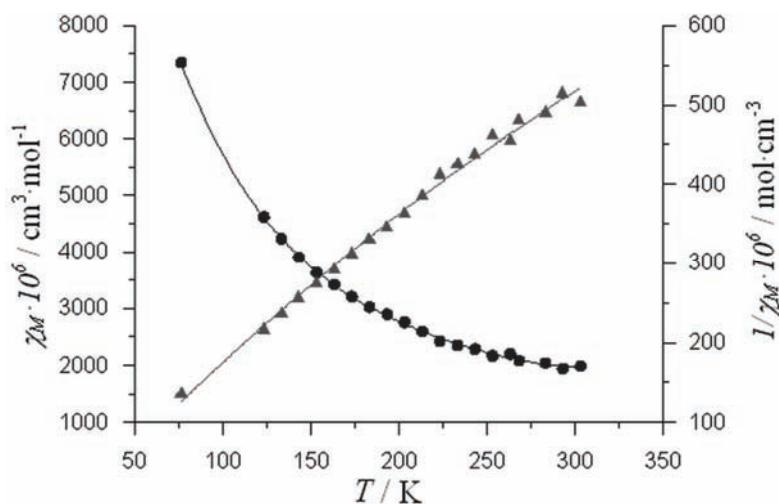


Fig. 4. Dependence between the magnetic susceptibility values vs. temperature for $[\text{CuC}_{20}\text{H}_{22}\text{N}_2\text{O}_6]$ (**1**).

CONCLUSIONS

The analytical data showed the presence of one metal ion per Schiff base ligand molecule and suggested a mononuclear structure for the Cu(II) and Ni(II) complexes obtained as microcrystalline powder. The complexes **1**, **2** and **3** are anhydrous compounds, whereas **4** contains one molecule of coordinated water, which is lost at 413–433 K. The TG and DTG data of the copper(II) complexes revealed that their decomposition patterns are different. The complexes **1–3** exhibit only a one-step decomposition, whereas a two-stage decomposition was observed in the case of complex **4**. The final products of complex decomposition were identified as CuO and NiO, respectively. The susceptibilities of all compounds closely follow the Curie law, but the magnetic moments of **1** and **3** are

slightly larger than that of **4**. This may indicate that the orbital contribution in **1** and **3** is higher than in **4**.

ИЗВОД

СПЕКТРАЛНА, ТЕРМАЛНА И МАГНЕТНА СВОЈСТВА КОМПЛЕКСА БАКРА(II) И НИКЛА(II) СА ШИФОВИМ БАЗАМА КАО ЛИГАНДИМА

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Синтетизовани су мононуклеарни комплекси бакара(II) и никла(II) опште формуле $[\text{Cu}(\text{L}^1)]$ (**1**), $[\text{Ni}(\text{L}^1)]$ (**2**), $[\text{Cu}(\text{L}^2)]$ (**3**) и $[\text{Cu}(\text{L}^3)\text{H}_2\text{O}]$ (**4**) (где је $\text{L}^1 = N,N'$ -етиленбис(4,6-диметоксисалицилиденаминато), $\text{L}^2 = N,N'$ -етиленбис(5-бромосалицилиденаминато), $\text{L}^3 = N,N'$ -етиленбис(5-бромо-3-метоксисалицилиденаминато)). Комплекси су кристалисали у облику монокристалног праха и за њихову карактеризацију употребљени су IR спектроскопија, термална анализа и магнетна мерења. Магнетна суцептибилност бакара(II) комплекса се мења са температуром у складу са Кири-Вајсовим (*Curie-Weiss*) законом. Магнетни моменти (μ_B) испитиваних комплекса на 303 K су: 2.29 (**1**), 2.20 (**3**) и 1.88 (**4**). Свака од наведених вредности се не мења са снижавањем температуре на 77 K. Комплекс никла(II) (**2**) је дијамагнетичан.

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