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In memoriam prof. dr. Ioan A. Silberg

SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF METAL COMPLEXES WITH AN AZO-DYE AS LIGAND

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ABSTRACT. The Cu(II), Co(II) and Ni(II) metal complexes derived from 1-(4'-hydroxy-6'-methyl-pyrimidin-2'-yl)-3-methyl-4-(4''-nitrophenylazo)-pyrazolin-5-one were synthesized and characterized by elemental analysis, thermogravimmetry, as well as by FT-IR, UV-VIS and ESR spectrometry. The results indicate that the organic compound act as a bidentate ligand *via* the nitrogen of azo group and the oxygen bound to the pyrazole ring. All complexes correspond to the molar ratio M : L : H_2O = 1 : 2 : 8. The local symmetry around the metal ions is pseudotetrahedral.

Keywords: *azo dyes, metal complexes, thermal behaviour, spectroscopic studies, 5-pyrazolone derivatives*

INTRODUCTION

Pyrazolin-5-one azo derivatives and their complexes with several metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Fe^{2+} etc.) are important pigments for vinyl polymers and synthetic leather or dyes for textile [1 - 4]. The metal complexes of 5-pyrazolone derivatives applied also as analytical reagents for microdetremination of metals [5, 6]. Over the past years the complexes of azo dyes have drawn the attention of many researchers [7 - 10]. Recently, a series of 1-pyrimidinyl analogs of the azocoupling products of 1-phenyl-3-methyl-pyrazolin-5-one has been prepared [11 - 13]. We intend to study the complexation of these new ligands with transition metal ions.

The present paper describes the synthesis and the structural investigation of three new metal complexes (**1 - 3)** obtained by the reaction of 1-(4'-hydroxy-6'-methyl-pyrimidin-2'-yl)-3-methyl-4-(4''-nitrophenylazo)-pyrazolin-5-one (**4**) (**H-PNPhP)** with Cu (II), Co (II) and Ni (II) ions (Scheme 1).

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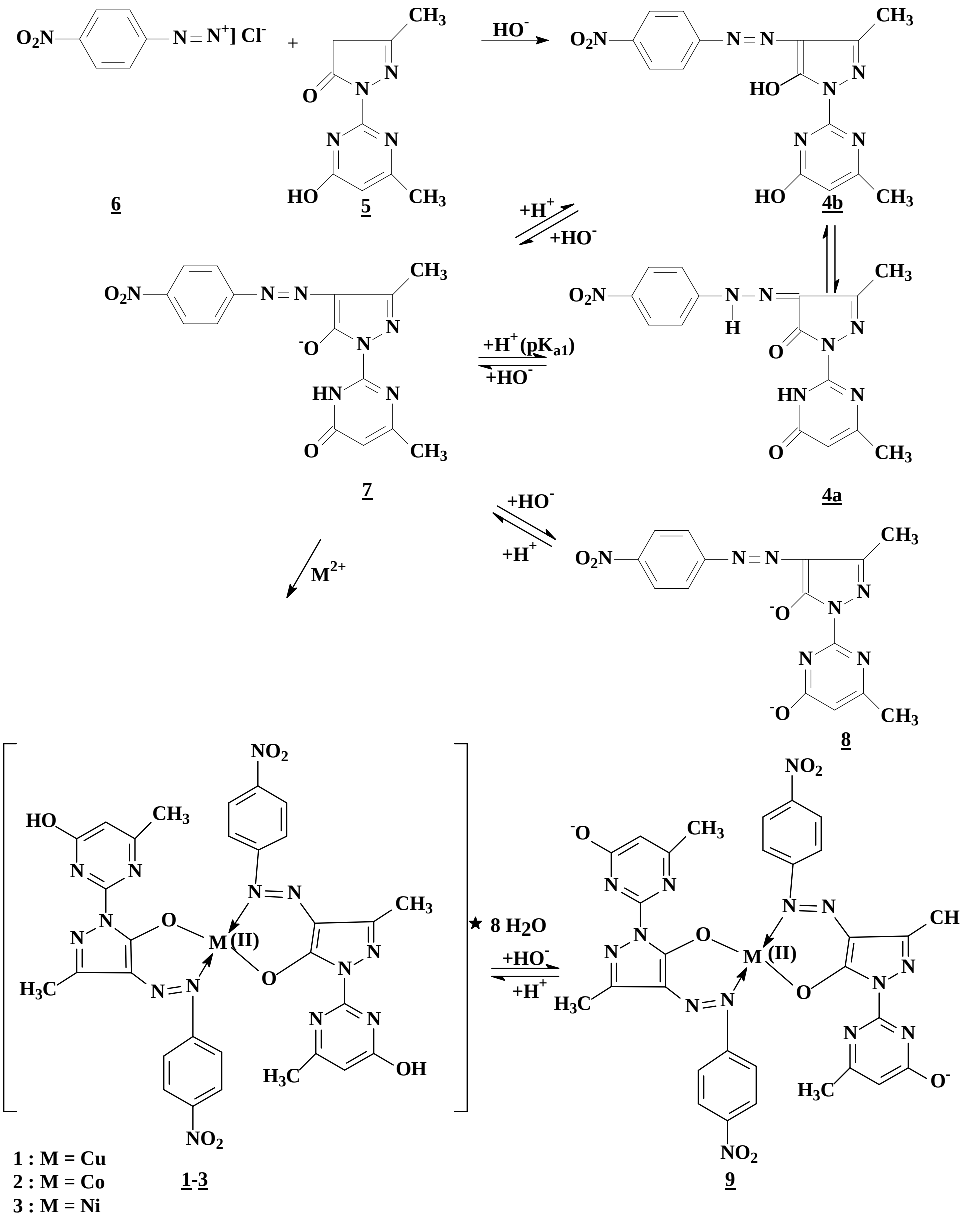


Scheme 1

RESULTS AND DISSCUSION

*The structure of the ligand (**4**)*

The azocoupling product (**4**) has several azo- and hydrazone-tautomeric forms (e.g. **4a**, **4b**) [11, 13 - 15]. According to our previous spectral studies [13, 15] the ligand (**4**) appears as a hydrazone tautomer (**4a**) in common solvents (e.g. acetic acid, methanol, benzene, chloroform, aqueous or acidulate ethanol) which is also in good agreement with other literature data on the azocoupling products of pyrazolin-5-one derivatives [9, 10, 12, 16 - 19]. In certain solvents, such as alkalized ethanol or DMF the ligand (**4**), is probably deprotonated similar to other pyrazolin-5-one azocoupling products [9, 13, 15, 18 - 20]. The deprotonation of ligand was confirmed by the pH dependence of the UV-VIS absorption spectra of isomolar solutions of (**4**) recorded in aqueous ethanol (1v/1v).

The absorption curves set, corresponding each to a certain pH-range: a) 2.87 - 8.19 (Fig. 1a) and b) 9.50 - 12.80 (Fig. 1b) show the same isosbestic points that indicate an equilibrium [1, 16, 18 - 22]. The absorbance *vs.* pH at the analytical wavelength for (**4**) (Fig. 2) generates two sigmoidal curves that are characteristic to the acid-base equilibrium [1, 21]. The two sigmoidal curves indicate two acid dissociation steps [20], corresponding to a dibasic acid AH_2, which is compatible with the structure (**4**), which has two mobile acidic hydrogens (Scheme 1).

By derivation of the sigmoidal curves two pKa values are obtained, *i.e.* $pKa_1 = 5.84$ and $pKa_2 = 10.56$. The species (**4a**), (**7**), (**8**) involved in the equilibrium are characterized by different absorption bands registered at 412, 442 and 490 nm.

The identification of the forms that are present in the basic medium is important because even these forms (**7** or **8**) will react with the metal ions.

As it is known other pyrazolin-5-one azocoupling products participate by complexation act as a bidentate ligand *via* the nitrogen of the azo group and the oxygen bound to the pyrazole ring [1, 6, 8 - 10]. In the case of the ligand (**4**), this oxygen atom should be corresponding to the form (**7**) or (**8**).

The structure of the metal complexes

The complexation reaction of Cu(II), Co(II) and Ni(II) salts with the ligand solution in each case yields a solid product. Higher melting points of these products as well as their different colours when compared to that of the ligand (**4**), indicate the formation of metal complexes. All complexes are coloured, microcrystalline and stable at room temperature. The complexes are insoluble in water and most usual organic solvents (chloroform, acetone, benzene, alcohol) but soluble in DMF.

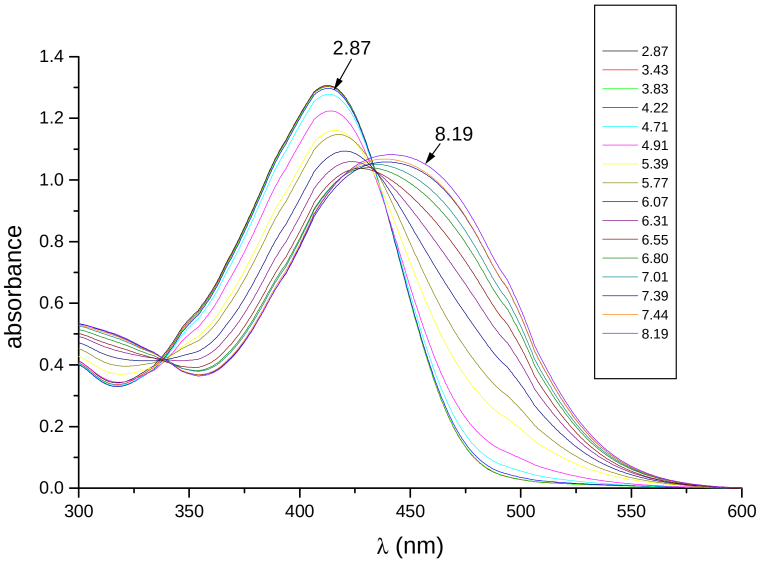


Figure 1a

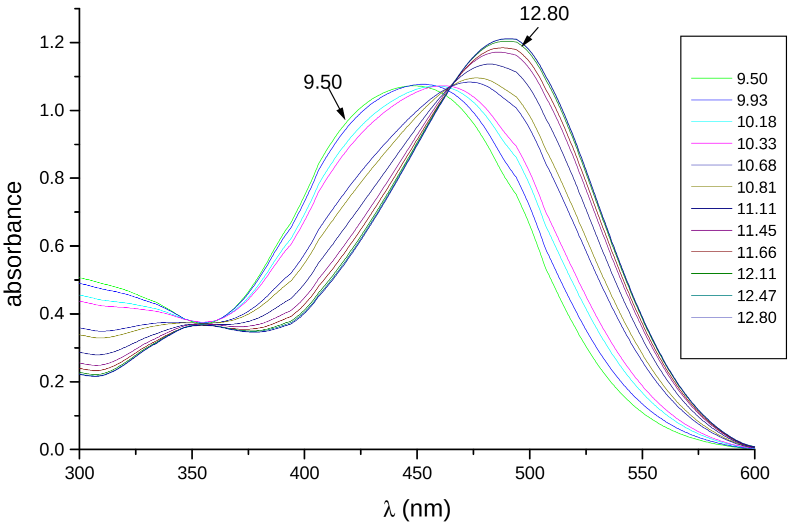


Figure 1b

Figure 1. The pH' dependence of the UV-VIS spectra of the isomolar solutions of (**<u>4</u>**) (c = 2.25 x 10^{-5} mol/L) in ethanol-water (1v/1v) at ionic strength of 0.01 mol/L KCl at 25^{0}C, in the pH' range 2.87-8.19 (1a), respectively 9.50-12.80 (1b).

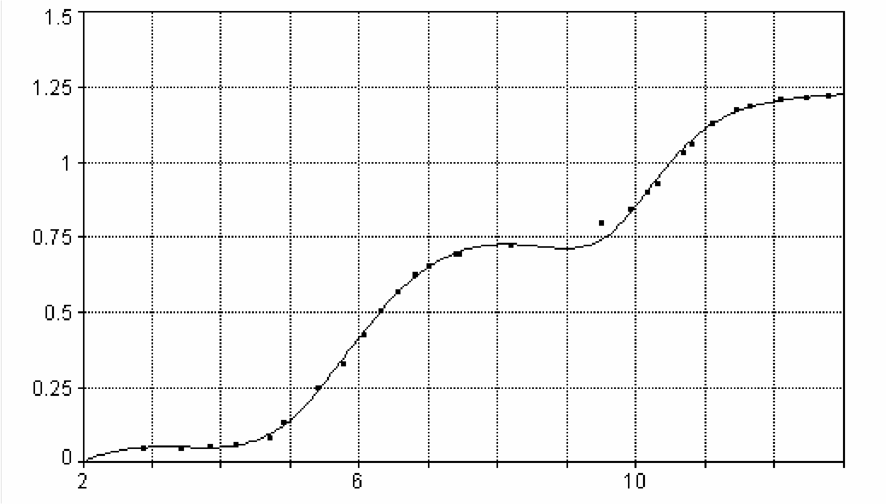


Figure 2.The plot absorbance at 490 nm *vs*. pH' corresponding to the spectra from Figure1

Some physico-chemical and elemental analysis data of the ligand (**4**) and its metal complexes (**1 - 3**) are given in Table 1 - 3.

The elemental analysis data (Table 1) and thermal analysis data (Table 3) indicate the molar ratio M : L : H_2O = 1 : 2 : 8, for each complex.

The UV-VIS spectra in DMF for the complexes (**1** - **3**) (Table 1) indicate a small hypsochromic shift and a low hypochromic effect comparative to the spectrum of the initial ligand (**4**), like the other similar complexes [9]. Since in DMF the UV-VIS spectrum of the ligand (**4**) (Table 1) corresponds to the dianion (**8**) (Fig. 1b) and the spectra of the complexes are only slightly shifted hipsochromically, the structure of the complexes in DMF solution should be (**9**), a situation that is to be expected for the initial structure (**1** - **3**) of the complexes in the presence of the basic impurities from DMF [17].

The structures (**1** - **3**) of the complexes are supported also by the fact that their UV-VIS spectra in ethanol correspond to the UV-VIS spectrum of more (**7**) or less (**4a**) deprotonated ligand (Fig.1a). Such a participation of the monodeprotonated species of pyrazolin-5-one azocoupling products to the complexation of metal ions occurs usually [9].

The IR spectra of the metal complexes (**1** - **3**) (Table 2) comparative to the free ligand supported these structures.

Table 1

Physico-chemical and elemental analysis data of the ligand (**4**) and metal complexes (**1** - **3**)

Compound		$C_{15}H_{13}N_7O_4$ (**4**)	$C_{30}H_{40}CuN_{14}O_{16}$ (**1**)	$C_{30}H_{40}CoN_{14}O_{16}$ (**2**)	$C_{30}H_{40}NiN_{14}O_{16}$ (**3**)
Molec. Weight		355.31	916.28	911.64	911.39
Yield [%]		73.21	64.85	63.67	51.98
Colour		orange	brown-yellow	brown-red	purple
Melting point [°C]		310	340	350	380
Visible absorption spectrum data, in DMF	$\Lambda_{max.}$ (nm)	486	473.5	481.5	471.5
	ε	30,800	25,700	13,500	21,800
	A	0.8059	0.6655	0.5632	0.6815
Elemental analysis data [%] found. (calcd.)	C	51.12 (50.71)	38.57 (39.32)	39.42 (39.52)	39.14 (39.53)
	H	4.38 (3.69)	4.02 (4.39)	4.15 (4.42)	4.11 (4.42)
	N	27.47 (27.59)	21.04 (21.40)	21.37 (21.51)	21.01 (21.51)

Table 2

IR absorption bands (cm^{-1}) of the ligand (**4**) and its metal complexes (**1** - **3**)

Assignment [cm^{-1}]	$C_{15}H_{13}N_7O_4$ (**4**)	$C_{30}H_{40}CuN_{14}O_{16}$ (**1**)	$C_{30}H_{40}CoN_{14}O_{16}$ (**2**)	$C_{30}H_{40}NiN_{14}O_{16}$ (**3**)
$\nu_{OH,}$ ν_{O-H-O}	-	2912-3642	3283-3646	3282-3656
ν_{NH}	3309-3633	wide band	wide band	wide band
$\nu_{C=O*}$	1696	-	-	-
$\nu_{C=O**}$	1673	1635	1623	1627
$\nu_{C-NO2\ as.}$	1556	1519	1517	1518
$\nu_{C-NO2\ sim}$	1344	1334	1330	1331
ν_{M-N}	-	619	598	578
ν_{M-O}	-	472	473	476

* γ-lactam from the pyrazolin-5-one entity

** γ-lactam from the pyrimidin-2-one entity

The absorption band of the free ligand (**4**) at 1696 cm^{-1}, that may be assigned to the stretching $\nu_{C=O}$ vibration of γ-lactam type [23] from the pyrazolin-5-one entity, is not registered in the IR spectra of the metal complexes (Table 2). This is caused by the fact that in these complexes the ligand participates as anion (**7**) analogous to other similar ligands [9]. The anions of the azocoupling products able of azo-hydrazone tautomerism have an azostructure (*e.g.* **7**) in which the pyrazolin-5-one >C=O group is transformed in $>C\text{-}O^{-}$ group. But in complexes (**1** - **3**) as well as in the ligand (**4**), an other band is present in the range 1620 - 1675 cm^{-1} which may be assigned to a stretching $\nu_{C=O}$ vibration of lactam type, namely a hexaatomic pyrimidin-one lactam [23]. The pyrimidin-2-one lactam form in the compounds (**4**) and (**1** - **3**) is possible on the basis of lactam- lactimic tautomerism of their 4-hydroxy-6- methyl-pyrimid-2-yl entity.

Another proof for the formation of the complexes are the new bands appearing in the range 472 - 476 cm^{-1}, which correspond to stretching $\nu_{M\text{-}O}$, vibration and in the range 578 - 619 cm^{-1}, which could be assigned to stretching $\nu_{M\text{-}N}$ vibration [6, 9].

Thermal investigation

The thermal behaviours of the ligand (**4**) and its metal complexes (**1** - **3**) are summarized in Table 3.

The thermogravimetric analysis indicated that the ligand (**H-PNPhP**) is anhydrous and the decomposition involved two steps.

In the temperature range 300 – 320°C an endothermic peak at 310°C indicated the melting point of the ligand in good agreement to the literature data [11].

The first decomposition step occurred in the temperature range 320 – 360°C and it has been accompanied by a strong exothermic effect (see the maximum peak at 340°C) with the loss of $C_6H_4NO_2$ rest.

The second step occurred in the temperature range 480 – 600°C, with an exo peak at 543°C which indicates the pyrolysis of organic rest.

The recorded mass loss of 65.63% is in good agreement to the calculated data (65.15%).

The aim of the thermal analysis of the metal complexes is to obtain information concerning their thermal stability of these and to decide whether the water molecules are inside or outside the coordination sphere.

The decompositions of each metal complex occur in three steps. The first step is characterized by an endothermic peak at 115°C for the Cu(II) complex, at 130°C for the Co(II) complex and at 125°C for the Ni(II) complex and corresponds to the loss of water molecules (see also the ESR results).

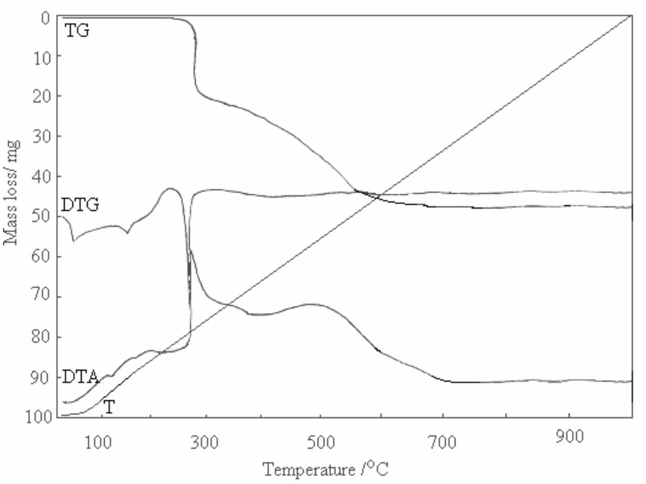
A comparison between the thermal behaviour of the ligand (**H-PNPhP**) and its metal complexes reveals that the melting points are growing up with the complexation. An endo peak in the DTA curves at 340°C for the Cu(II) complex, at 350°C for the Co(II) complex and at 380°C for the Ni(II) complex corresponds to the melting points. This phenomenon proves that the thermal stability is increased by the formation of coordination compounds with M-N and M-O bonds. The second step is accompanied by a strong exothermal effect and corresponds to the loss of 2 mole of $C_6H_4NO_2$ rest of each metal complex.

Table 3

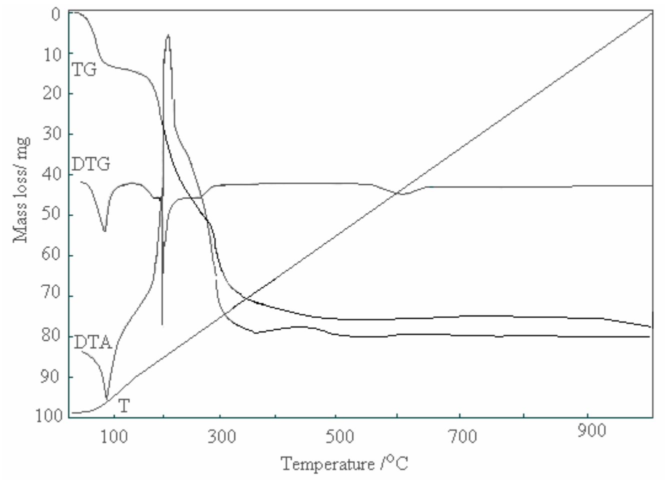
Thermogravimetric analysis results of the ligand H-PNPhP (**<u>4</u>**) and its metal complexes (**<u>1</u>** - **<u>3</u>**)

Compound	Temp. range [^{O}C]	DTA peak [^{O}C]		TG weight loss [%]		Assignment
		Endo	Exo	Calcd.	Exp.	
H-PNPhP (**<u>4</u>**)	300-320	310	-	-	-	melting point
	320-360	-	340	34.36	35.84	- loss of $C_6H_4NO_2$ rest
	480-600	-	543	65.64	64.15	- pyrolysis of organic rest
$[Cu(C_{15}H_{12}N_7O_4)_2]$ •$8H_2O$(**<u>1</u>**)	80-160	110	-	15.72	15.23	- 8 mole of hydrating water
	320-380	340	-	-	-	melting point
		-	375	31.62	32.38	- loss of 2 $C_6H_4NO_2$ rest
	400-460	-	440	34.04	43.28	- pyrolysis of organic rest
		-	-	18.88	18.09	CuO residue
$[Co(C_{15}H_{12}N_7O_4)_2]$ •$8H_2O$(**<u>2</u>**)	100-200	130	-	15.80	15.89	- 8 mole of hydrating water
	340-420	350	-	-	-	melting point
		-	380	31.81	31.68	- loss of 2 $C_6H_4NO_2$ rest
	420-560	-	425	42.17	41.45	- pyrolysis of organic rest
		-	-	10.22	10.98	CoO residue
$[Ni(C_{15}H_{12}N_7O_4)_2]$ •$8H_2O$(**<u>3</u>**)	80-180	125	-	15.80	15.72	- 8 mole of hydrating water
	360-440	380	-	-	-	melting point
		-	405	31.82	32.35	- loss of 2 $C_6H_4NO_2$rest
	440-580	-	450	39.80	40.18	- pyrolysis of organic rest
		-	-	12.58	11.75	NiO residue

Above 420^{o}C a broad exothermic peak indicate the last step which correspond to the pyrolysis of the organic rest. The final products of the pyrolysis are metal oxide with the stoichiometric ratio M : O = 1:1. Figure 3 displays the derivatograms of the ligand (**H-PNPhP**) and its Cu(II) complex (**<u>1</u>**).



a-H-PNPhP(<u>**4**</u>).



b-$[Cu(C_{15}H_{12}N_7O_4)_2]\bullet 8H_2O$(**1**)

Figure 3. The simultaneous TG, DTG and DTA curves obtained by derivatograph for a- H-PNPhP (**4**) (sample mass = 50mg) and b-$[Cu(C_{15}H_{12}N_7O_4)_2]\bullet 8H_2O$(**1**) (sample mass=100mg)

ESR spectra and magnetic properties

The powder ESR spectrum of $[Cu(C_{15}H_{12}N_7O_4)_2]\bullet 8H_2O$(**1**), complex at room temperature (Fig. 4) is typical for monomeric species with pseudotetrahedral local symmetry around the metal ion. The principal values of the g tensor (g_{II}= 2.178, $g_{\perp}$= 2.117) correspond to a CuN_2O_2

chromophore [24]. The ordering of g values indicates the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital. The calculated g_{av} =2.137 value show a considerable covalent character of the complex [25]. The shape and the g values ($g_{\parallel}$= 2.213, $g_{\perp}$= 2.026) for the Co(II) complex are typical for pseudotetrahedral species.

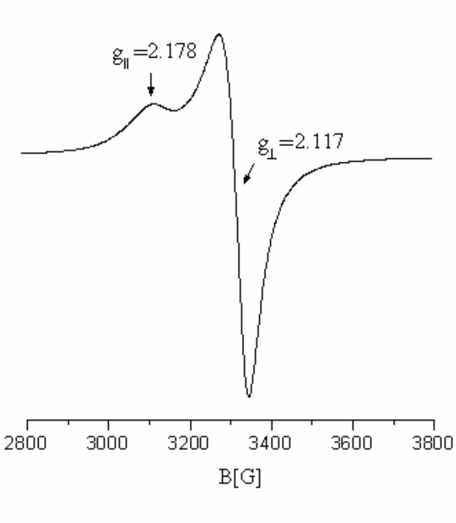


Figure 4. Powder ESR spectrum of $[Cu(C_{15}H_{12}N_7O_4)_2]•8H_2O$(**1**) complex at room temperature

The magnetic susceptibility measurements indicate a Curie-Weiss behaviour (Fig. 5) with values of magnetic moments specific to monomeric species. The values of magnetic moments were calculated considering also the temperature independent contribution. The magnetic moments (μ_{eff}=1.91 μ_B, μ_{eff}=5.21 μ_B, μ_{eff}=3.21 μ_B for Cu(II), Co(II) and Ni(II) complexes) confirm the pseudotetrahedral local symmetries around the metallic ions [26].

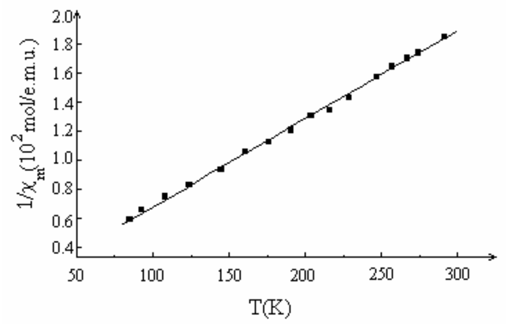


Figure 5. Temperature dependence of $1/\chi_m$ for $[Cu(C_{15}H_{12}N_7O_4)_2]•8H_2O$(**1**)

EXPERIMENTAL PART

Materials and instrumentation

All reagents and chemicals were purchased from commercial sources and used as received. Elemental analyses were carried out at the Vario El III CHNS-analyzer. The electronic absorption spectra were performed on Jasco V-530-UV-VIS spectrophotometer. The IR spectra were recorded in KBr pellets with a FT-IR-615-spectrophotometer. The thermoanalytical curves were recorded on an OD-103 MOM derivatograph. The samples were heated at a constant rate of 5^oC min^{-1} from 20-1000^oC. Al_2O_3 was used as reference material in static air atmosphere. Powder ESR spectra at room temperature were recorded at 9.4 GHz (X band) using standard JEOL-RES-3S equipment. Magnetic susceptibility measurements were made on powdered samples with a Faraday balance.

Synthesis of the metal complexes

The azocoupling product (**4**) was prepared by using a standard procedure from 1-(4'-hydoxy-6'-methyl-pyrimidin-2'-yl)-3-methyl-pyrazolin-5-one (**5**) and 4-nitrobenzenediazonium salt (**6**) [11 - 14]. The metal complexes (**1** - **3**) were synthesized by the following procedure: to a suspension of ligand (**4**) (1mmol) in 50 mL methanol was slowly added with stirring a solution of tetra-n-butylammonium hydroxide until the azocoupling product is completely dissolved. To this solution of ligand was added slowly, dropwise, a solution of the metal salt [$CuSO_4$•$5H_2O$, $Co(NO_3)_2$ •$6H_2O$, $Ni(NO_3)_2$•$6H_2O$] (0.5 mmol) in distilled water. The mixture was stirred for 2h. After standing at room temperature for 16h, the resulted precipitate was vacuum filtrated and washed on the filter with distilled water and methanol, dried in air 48h and kept in dark bottles.

CONCLUSIONS

The ligand (**4**) and its Cu(II), Co(II) and Ni(II) complexes (**1** - **3**) were characterized by elemental analysis, thermal behaviour and spectral studies. The results are in agreement with the corresponding formulae: $C_{15}H_{13}N_7O_4$(**4**), $[Cu(C_{15}H_{12}N_7O_4)_2]$•$8H_2O$(**1**), $[Co(C_{15}H_{12}N_7O_4)_2]$•$8H_2O$(**2**), respectively $[Ni(C_{15}H_{12}N_7O_4)_2$•$8H_2O]$(**3**).

The IR and UV-VIS spectra indicated that the organic compound act as a bidentate ligand *via* the nitrogen of the azo group and the oxygen bound to the pyrazole ring.

The greater value of the melting point for complexes, as compared to the free ligand indicates that thermal stability is increased by the formation of complexes with M-N and M-O bonds.

The ESR spectra and magnetic susceptibility measurements confirm the pseudotetrahedral local symmetries around the metal ions.

ACKNOWLEDGEMENT

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