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DIVALENT TRANSITION METAL COMPLEXES
4-(4-ethoxy-phenylhydrazono)-1-phenyl-3-methyl-1H-pyrazolin-5(4H)-one

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4-(4-ethoxy-phenylhydrazono)-1-phenyl-3-methyl-1H-pyrazolin-5(4H)-one (**5a**) (H-EMPhP) as ligand and its Cu(II), Co(II) and Ni(II) complexes **4**(**a**–**c**) were synthesized and characterized by their thermal and spectral properties. The azocoupling product (H-EMPhP), able of azo-hydrazone tautomerism **5**(**a**–**d**), act as a bidentate ligand involving in coordination the azogroup nitrogen of its common anion (**7**) and the oxygen atom that is bound to the pyrazole ring of the mentioned anion (**7**).

Keywords: *azocoupling products, metal complexes, 1-phenyl-3-methyl-1H-pyrazolin-5-one, spectroscopic studies, thermal behaviour*

Introduction

From 1900 [1, 2] until the present [3–6] the derivatives of several metal ions (Cr^{3+}, Cu^{2+}, etc.) with a series of azocoupling products (**1**) between 1-phenyl-3-methyl-pyrazolin-5-one (**2**) and the aromatic diazonium salts (**3**) are applied as dyes for textile. This fact stimulated the permanent search [1–10] for such new metal complexes of the dyes (**1**). Concomitantly the corresponding studies have contributed to the elucidation of the structure [2, 3, 7–10] of the metal complexes of these dyes and have supported [9, 10] the azo-hydrazone tautomerism of the dyes (**1**).

This work, that presents the synthesis, the spectroscopic and thermogravimetric investigation of the reaction products **4**(**a**–**c**) between 4-(4-ethoxyphenylhydrazono)-1-phenyl-3-methyl-1H-pyrazolin-5(4H)-one (H-EMPhP) (**5a**) and the Cu(II), Co(II) and Ni(II) ions (Scheme 1), has the same objectives as the above quoted studies.

Experimental

The diazotation of the 4-ethoxyaniline and the azocoupling of the obtained diazonium salt (**6**) with 1-phenyl-3-methyl-pyrazolin-5-one (**2**) was achieved by known standard methods [3, 11].

The metal complexes were synthesized by the following procedure: to a suspension of ligand (**5a**) (1 mmole) in 50 mL methanol was slowly added with stirring, a dilute solution of NaOH until the azocoupling product (**5a**) is completely dissolved (at pH=10–10.5). A solution of the metal nitrate (0.5 mmole) [$Cu(NO_3)_2\cdot3H_2O$, $Co(NO_3)_2\cdot6H_2O$ or $Ni(NO_3)_2\cdot6H_2O$] in distilled water were mixed with the ligand solution under stirring. The pH modify by self at 5–5.5 to the Cu(II) complex, at 6–7 to the Co(II) complex and at 7.5–8 to the Ni(II) complex. After standing at room temperature overnight, the resulted precipitate was filtered and washed with dilute NaOH solution, distilled water and methanol.

Some physico-chemical and elemental analysis data of the synthesized ligand (**5a**) and of its metal complexes **4**(**a**–**c**) are given in Table 1.

Melting points were recorded with an Electrothermal IA 6304 apparatus and are uncorrected. Elemental analyses were carried out at the Perkin Elmer 240 analyzer. The electronic absorption spectra were performed on a Specord UV-VIS spectrophotometer. The ^1H-NMR spectrum was recorded in $CDCl_3$, at room temperature on a Varian Gemini 300 (300 MHz) apparatus. 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°C min^{-1}, reference material Al_2O_3, and atmosphere: static air. The sensitivity on the galvanometers was TG=100 mg, DTG=1/5, DTA=1/5. ESR spectra were recorded at 9.4 GHz (X band) at room temperature, using standard JEOL-JES-3B equipment.

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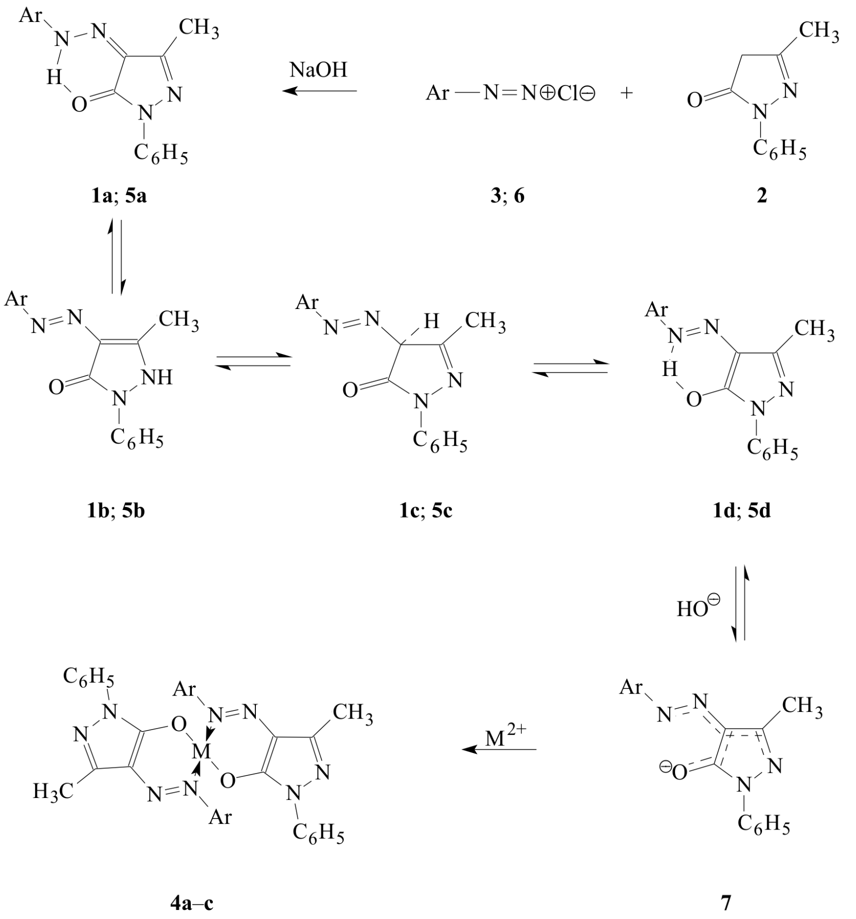
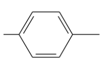


1a–**d**; **3**: *Ar*=aryl

4a–**c**; **5a**–**d**; **6**; **7**: *Ar*=CH_3CH_2O– 

4a: *M*=Cu; **4b**: *M*=Co; **4c**: *M*=Ni

Scheme 1

Table 1 Physico-chemical and elemental analysis data of the synthesized ligand and metal complexes

Compound		$C_{18}H_{18}N_4O_2$ (**5a**)	$C_{36}H_{38}CuN_8O_6$ (**4a**)	$C_{36}H_{38}CoN_8O_6$ (**4b**)	$C_{36}H_{38}NiN_8O_6$ (**4c**)
Molecular mass		322.36	742.29	737.69	737.43
Yield/%		87.00	72.97	88.32	86.41
Colour		orange	dark-brown	ochre	brown-red
Melting point/°C		156–157	244–245	303–304	210–211
Visible absorption spectrum data, in methanol	Λ_{max}/nm	423	413	411	409
	ε	25000	22000	26000	28000
Elemental analysis data/% found (calcd.)	M	– –	8.99 (8.55)	7.63 (7.98)	8.32 (7.95)
	C	66.63 (67.06)	58.78 (58.25)	58.70 (58.61)	59.16 (58.63)
	H	4.96 (5.62)	4.85 (5.15)	4.49 (5.19)	4.67 (5.19)
	N	16.95 (17.37)	14.48 (15.18)	14.64 (15.18)	14.69 (15.19)

Results and discussion

*The synthesis and the structure of the ligand (**5**)*

The obtaining of a colored product with a single, intense and sharp absorption band in visible region (Table 1) by reaction between (**2**) and (**6**) shows that the azocoupling really occurs, because the starting compounds are colorless. Elemental analysis and ^{1}H-NMR confirm the formation of 1:1 azocoupling product (**5**). Thus, in the ^{1}H-NMR spectrum in $CDCl_3$ of the (**5**) appears a singlet at 2.37 ppm owing to the protons of the methyl group from the position 3 of a single pyrazolin-5-one moiety [11, 12] and a triplet centred at 1.44 ppm with an intensity corresponding also to three protons. The coupling constant of this triplet (J=6.8 Hz) is found also by the quartet centred at 4.05 ppm and having an intensity corresponding to two protons. These data indicate that the mentioned triplet and quartet must correspond [13] to the ethoxy group bound to the benzene ring. Such a group in (**5**) can originate only from a single rest of diazocomponent (**6**).

On the other hand the ^{1}H-NMR spectrum of (**5**) shows, as for other similar azocoupling products (**1**) [11, 12, 14, 15], the formal presence of only one species although for all these (**1**, **5**) are to expect [14, 15] four tautomeric forms: (**1a**–**1d**), respectively (**5a**–**5d**). The only one species detected for the dyes (**1**) has been proved to be [11, 12, 14, 15] the hydrazone one (**1a**). Characteristic for this hydrazone form (**1a**) of the dyes (**1**) is the presence in the ^{1}H-NMR spectra of a signal at a very low field (δ=13–14 ppm) owing to the mobile hydrogen atom of the hydrazone NH group [11, 12, 14, 15]. Since in the ^{1}H-NMR spectrum of (**5**) is present a such down field signal at 13.73 ppm as singlet and with an intensity that correspond to one proton – we assigne the hydrazone tautomer structure (**5a**) for the ligand used in this study. But in alkaline media – in which the ligand (**5a**) reacts with metal ions – it is to expect [3, 16–19] that the ligand should be converted into a common azoanion (**7**). In fact even this anion (**7**) should react with metal ions to form the metal complexes **4**(**a**–**c**) [8, 9] (Scheme 1).

*The synthesis and the structure of the metal complexes **4**(**a**–**c**)*

The isolation of precipitates different colored relative to the orange ligand as a result of the reaction of this (**5a**) with the metal ions M^{2+} in alkalized aqueous methanol, may indicate the formation of complexes. The different and much higher melting points of the isolated precipitates support the obtainment of complexes. Their elemental analysis is in agreement with an approximately composition metal:ligand of 1:2, that has been found also by certain metal complexes with other similar ligands to (**5**) [8, 9].

In exchange the elemental analysis data are much corresponding for 1:2 metal:ligand complexes hydrated with two water molecules (see also the thermal analysis data).

The visible absorption bands of the complexes **4**(**a**–**c**) are broader and slightly hypsochromically shifted comparative to the corresponding band of the ligand (**5a**). Because also in the anion of the ligand (**7**) is observed a hypsochromically shift and a broadening of the visible absorption band with respect to that of the ligand (**5a**) the above effects in visible spectra of complexes **4**(**a**–**c**) may support the participation as anion (**7**) (EMPhP) of the ligand (**5a**) in complexes **4**(**a**–**c**). Otherwise this assumption is very reasonable [8, 9].

The bonding of the ligand to different metal ions was investigated also by comparing the IR spectrum of the free ligand with those of the metal complexes. IR spectrum of free ligand undergoes a certain modification when coordinated to a metal ion [20–22].

Partial assignments of the IR absorption bands observed for the free ligand and the metal complexes are given in Table 2.

In the spectral region 3380–3680 cm^{-1} a wide band formed by 2–3 overlapped bands is observed that may be assigned to ν_{OH} and $\nu_{O\text{–}H\text{–}O}$ vibration due to intra- and intermolecular hydrogen bonding in the crystalline state of metal complexes. The comparison of IR bands of free ligand H-EMPhP and its metal complexes shows a change in the region of $\nu_{C=O}$ and $\nu_{C=N}$ vibrations. These bands of the metal complexes **4a, 4c** were shifted to

Table 2 Some IR absorption bands (cm^{-1}) of the ligand H-EMPhP (**5a**) and its metal complexes **4**(**a**–**c**)

Assignment/cm^{-1}	H-EMPhP (**5a**)	$[Cu(EMPhP)_2]\cdot 2H_2O$ (**4a**)	$[Co(EMPhP)_2\cdot(H_2O)_2]$ (**4b**)	$[Ni(EMPhP)_2\cdot(H_2O)_2]$ (**4c**)
ν_{OH}, $\nu_{O\text{–}H\text{–}O}$	–	3386–3646	3375–3595	3388–3685
$\nu_{C=O}$	1650	1599	1654	1601
$\nu_{C=N*}$	1592	1559	1598	1557
$\nu_{C=N**}$	1548	1537	1545	1527
$\nu_{M\text{–}N}$	–	580	579	576
$\nu_{M\text{–}O}$	–	418–436	414–422	413–436

*from pyrazolonic ring
**exocyclic

Table 3 Thermal data of ligand H-EMPhP (**5a**) and its metal complexes **4**(**a–c**)

Compound	T_{range}/°C	DTA peak/°C		TG mass loss/%		Assignment
		endo	exo	calcd.	exp.	
H-EMPhP (**5a**)	20–320	157	–	–	–	melting point
		–	270	41.93	42.26	C_8H_9NO rest
	320–520	–	380	34.15	32.98	$C_4H_4N_3O$
	520–1000	–	620	23.91	23.71	pyrolysis of organic rest
$[Cu(EMPhP)_2]\cdot 2H_2O$ (**4a**)	20–320	125	–	4.85	4.08	2 mole of probably uncoordinated water
		244	–	–	–	melting point
		–	290	36.42	35.71	$2C_8H_9NO$ rest
	320–520	–	385	29.66	30.61	$2C_4H_4N_3O$ rest
	520–1000	–	643	20.77	21.42	pyrolysis of organic rest
		–	–	8.30	8.18	CuO residue
$[Co(EMPhP)_2\cdot(H_2O)_2]$ (**4b**)	20–320	160	–	4.88	4.59	2 mole of probably coordinated water
		303	–	–	–	melting point
	320–520	–	330	36.64	36.72	$2C_8H_9NO$ rest
		–	480	29.84	30.60	$2C_4H_4N_3O$ rest
	520–1000	–	540	20.90	20.40	pyrolysis of organic rest
		–	–	7.74	7.69	CoO residue
$[Ni(EMPhP)_2\cdot(H_2O)_2]$ (**4c**)	20–320	140	–	4.88	5.05	2 mole of probably coordinated water
		210	–	–	–	melting point
		–	280	36.66	35.35	$2C_8H_9NO$ rest
	320–520	–	380	29.85	30.30	$2C_4H_4N_3O$ rest
	520–1000	–	580	20.9	20.20	pyrolysis of organic rest
		–	–	7.70	9.10	NiO residue

lower value due to chelating with the metal ions. It is possible that even as a consequence of different structure of Co^{2+} (**4b**) complex with respect to the structures of Cu^{2+} (**4a**) and Ni^{2+} (**4c**) complexes (see also the ESR data) by the former complex (**4b**) is observed on opposite shift of the corresponding bands.

The new bands appearing in the range 576–580 cm^{-1} are assigned to $\nu_{M–N}$ while those at 413–436 cm^{-1} could be attributed to $\nu_{M–O}$ [20–22].

The powder ESR spectrum of Cu(II) complex at room temperature (Fig. 1) is typical of pseudo-tetrahedral monomeric species. The values $g_{\|}$=2.302 and $g_{\perp}$=2.054 correspond to a CuN_2O_2 chromophore [23]. The powder ESR spectrum of Co(II) complex is quasi-isotropic (g=2.069), characterizing monomeric species with octahedral environments. ESR spectrum of Ni(II) complex is almost isotropic (g=2.061). The presence of a weak signal at $g\approx 4$ suggests a small distortion of the octahedral symmetry around the metal ion.

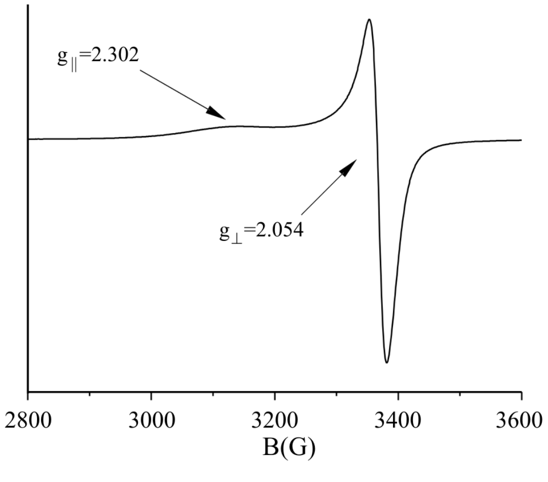


Fig. 1 Powder ESR spectrum of Cu(II) complex at room temperature

Thermal investigation

The thermal decomposition of the compounds was studied by means of a derivatograph in air atmosphere. Thermal stability domains, melting points, decomposition phenomena and their assignments are summarized in Table 3.

The interval 20–320°C is characterized by an endothermic peak at 157°C in the DTA curve of the ligand (H-EMPhP) where correspond to the melting point of the sample. Since the ligand (**5a**) is able ([3, 11, 14, 15, 18, 19]) of azo-hydrazone tautomerism it can appear also in the azoform even if only in traces. According to the literature data the azo bonds of the azo compounds are breaking when the temperature growing more than 250°C [24]. Probably results a nitro compound which is instantly evaporated or burned, that process being registered as a leap in the TG curve. The maximum exothermic effect in the DTA curve is at 270°C.

In the temperature range 320–520°C an exothermic peak at 380°C indicates the decomposition of phenyl-pyrazolin-5-one rest, corresponding to a net mass loss of 32.98%.

Above 520°C a broad exothermic peak indicates the pyrolysis of organic rest of the sample.

The metal complexes decompose progressively too.

Between 20–320°C the DTA curves indicated two endothermic peaks. The first is present at 125°C, for the Cu^{2+}-complex (**4a**), at 160°C for the Co^{2+}-complex (**4b**) and at 140°C for the Ni^{2+}-complex (**4c**) and it correspond to the loss of water. Very probable this water is uncoordinated for Cu^{2+}-complex (**4a**) and coordinated for Co^{2+} (**4b**) and Ni^{2+} (**4c**) complexes (see also the ESR results). The second endothermic peak situated in the DTA curves at 244°C (**4a**), respectively 303°C (**4b**) and 210°C (**4c**), (Table 1) correspond to the melting point of each complex. A comparison between the thermal behaviour of the free ligand and the complexes reveals that the melting point of the free ligand is lower than those of the complexes. This phenomenon proves that the thermal stability is increased by the formation of coordination compounds with M–N and M–O bonds.

The exothermic peak between 280–330°C for the metal complexes correspond to the breaking of the azo bonds.

Above 330°C two exothermic peaks indicate the decomposition of the rest of the sample. The final products of the pyrolysis are metal oxides in stoichiometric ratios (M:O=1:1). Figure 2 presents the derivatograms for ligand (**5a**) and its copper complex (**4a**).

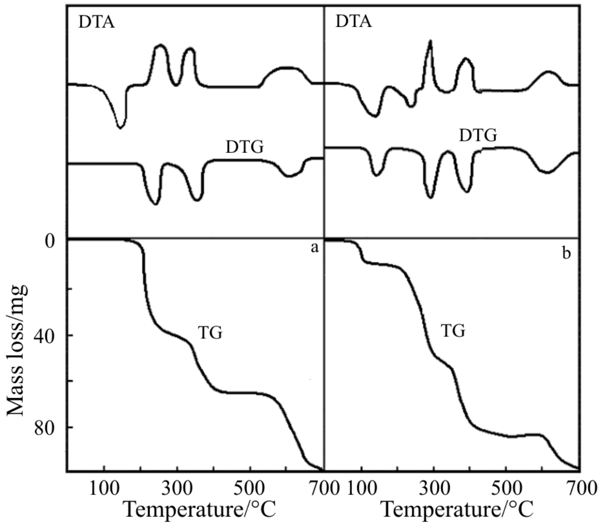


Fig. 2 The simultaneous TG, DTG and DTA curves obtained by a derivatograph for a – H-EMPhP and b – $[Cu(EMPhP)_2]\cdot 2H_2O$

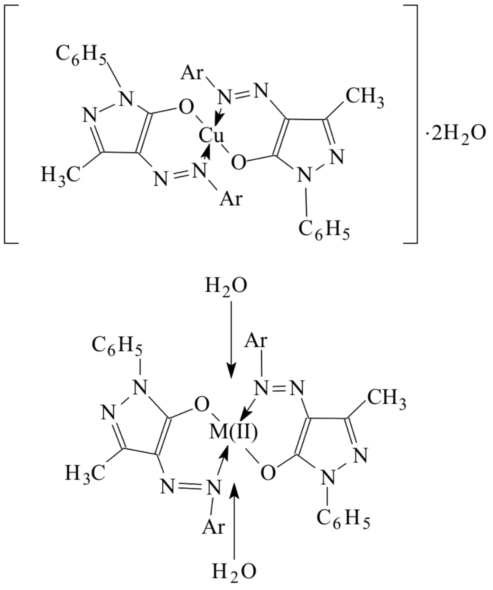
Conclusions

The obtained ligand (**5a**) and its complexes with divalent transition metals (**4a–c**) were characterized by spectroscopic and thermal behaviour over 20–1000°C temperature range that indicate their formula: $C_{18}H_{18}N_4O_2$ (**5a**), $[Cu(C_{18}H_{17}N_4O_2)_2]\cdot 2H_2O$ (**4a**), $[Co(C_{18}H_{17}N_4O_2)_2\cdot(H_2O)_2]$ (**4b**), respectively $[Ni(C_{18}H_{17}N_4O_2)_2\cdot(H_2O)_2]$ (**4c**).

The IR spectra show that the ligand act as a bidentate ligand with coordinating involving the nitrogen atom of the azo group and the oxygen atom that is bound to the pyrazole ring.

The ESR spectra confirm pseudotetrahedral [for the Cu(II) ion] and octahedral [for the Co(II) and Ni(II) ions] local symmetry.

We propose the following structure (Fig. 3) for the studied compounds.



M(II)=Co(II) or Ni(II)

Fig. 3 Suggested structure of the studied complexes

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