

## COORDINATION COMPOUNDS OF Cu(II), Ni(II), Zn(II) WITH 1-(2-METHYL-PHENYL)-PYRAZOLE-3,4-DICARBOXYLIC ACID

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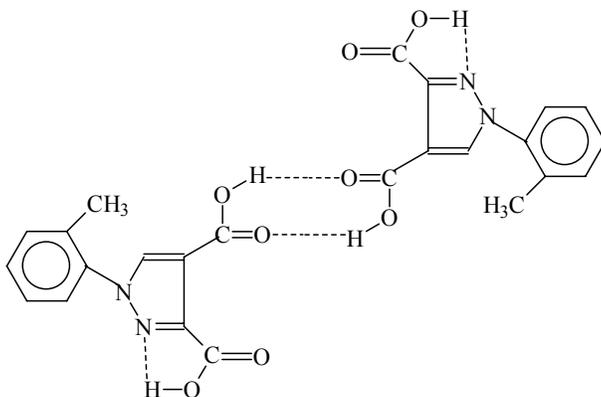
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The paper presents new complex compounds of some *3d* metals with 1-(2-methyl-phenyl)-pyrazole-3,4-dicarboxylic acid of the type  $ML_2(CH_3OH)_2$ , and  $ML_2(H_2O)_2$  where  $M(II) = Cu, Ni, Zn$ , which were characterized by elemental chemical and thermodifferential analysis, and electronic, IR and EPR spectra.

### INTRODUCTION

The interest in the study of the ability of pyrazole and of its derivatives to form coordination compounds with metal(II) ions may be explained by their potential applications as drugs. These might offer important data for understanding some of the reactions between the metallic ions and the natural or synthetic biologically active organic compounds. Our previous paper<sup>1</sup> has reported on the synthesis and characterization of the coordination compounds of some *3d* metals with the pyrazole derivative 1-phenyl-pyrazole-3,4-dicarboxylic acid.

The present work investigates whether or not the methyl substituent in the benzene ring has any influence on the resulting compounds type. The presence of the two carboxylic groups lying in vicinal position with respect to each other favours intermolecular hydrogen bond forming dimer structure and intramolecular hydrogen bond through pyridine nitrogen of the pyrazole ring and carboxylic group lying in vicinal position with respect to each other (Scheme 1)

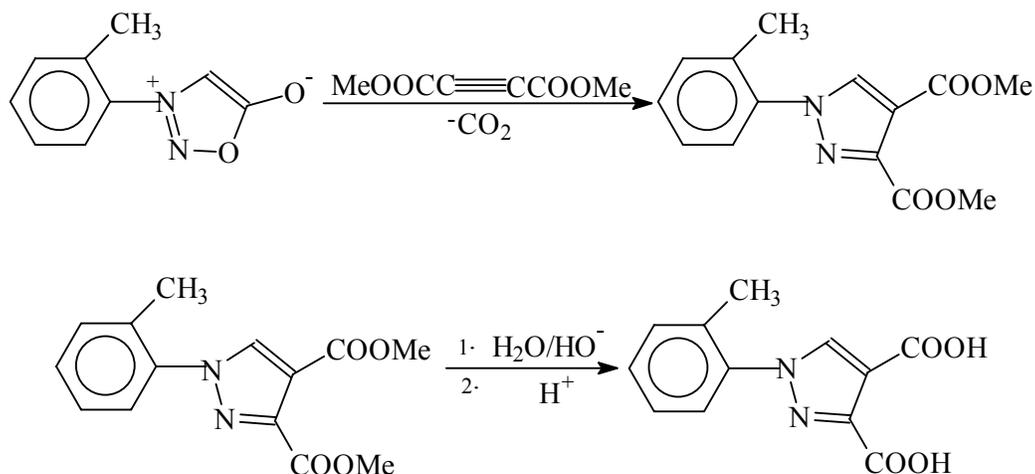


Scheme 1

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## RESULTS AND DISCUSSION

The ligand **L** was prepared from 3,4-dicarbomethoxy-1-(2-methyl-phenyl)-pyrazole under basic hydrolysis condition and its structure was confirmed by elemental analysis, IR and NMR spectroscopy. The diester was obtained by 1,3-dipolar cycloaddition reaction between 3-(2-methyl-phenyl)-sydnone and dimethyl acetylenedicarboxylate (Scheme 2).<sup>2-6</sup>



Scheme 2

Synthesis of the coordination compounds was performed in methanolic or aqueous solution by treating the solution of the metal(II) acetates (M= Cu, Ni, Zn) with the solution of the ligand in a molar ratio M: L= 1:2 or 1:4. Only complex compounds of the  $ML_2(CH_3OH)_2$  or  $ML_2(H_2O)_2$  type were obtained (Table 1).

Table 1

Analytical and physical data

No.	Compound	Formula	Colour	M.p. (°C)
1	$CuL_2(CH_3OH)_2$	$CuC_{26}H_{28}O_{10}N_4$	light blue	267-268
2	$NiL_2(CH_3OH)_2$	$Ni_2C_{26}H_{28}O_{10}N_4$	green	281-282
3	$ZnL_2(CH_3OH)_2$	$ZnC_{26}H_{28}O_{10}N_4$	white	238-240
4	$CuL_2(H_2O)_2$	$CuC_{24}H_{24}O_{10}N_4$	light blue	261-262
5	$NiL_2(H_2O)_2$	$NiC_{24}H_{24}O_{10}N_4$	light green	248-250
6	$ZnL_2(H_2O)_2$	$ZnC_{24}H_{24}O_{10}N_4$	white	230-232

The new compounds have been characterized by elemental and thermogravimetric analysis and electronic, IR spectra and for Cu(II) compounds by EPR spectra. The complex compounds were microcrystalline materials, stable in air. The complex compounds contain also two methanol or water molecules which can be either as coordinated methanol (water) or crystallization solvent.

**The thermogravimetric analysis** confirmed the formula of the compounds. The curves are similar. For compounds **2** and **3** (Table 1) the mass loss noticed within 190-270 °C and 180-270 °C range respectively on TG curve corresponds to the loss of two methanol molecules per molecule: found 10.56 %, requires for 2  $CH_3OH$  = 10.49 %, and found 10.89%; requires 10.79 %, respectively. The two methanol molecules act as ligands in these complex compounds.

**Electronic spectra.** Diffuse reflectance spectra of Cu(II) complex compounds **1** and **2**, (Table 2), present a broad absorption band centered at 760 nm, and 720 nm, respectively, and a shoulder at 700 nm, and 650 nm, respectively.

Table 2

Electronic spectral data and EPR spectral parameters

No	Compound	$\lambda_{\max}$	Assignments	$g_{\perp}$	$g_{\parallel}$
1	CuL <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub>	760; 700 sh	<i>d-d</i>	2.075	2.210
2	CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	720; 650 sh	<i>d-d</i>	2.139	1.980
3	NiL <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub>	980	<sup>3</sup> T <sub>1g</sub> ← <sup>3</sup> A <sub>2g</sub> )	-	-
		650; 760	<sup>3</sup> T <sub>2g</sub> (F)← <sup>3</sup> A <sub>2g</sub> <sup>1</sup> E <sub>g</sub> ← <sup>3</sup> A <sub>2g</sub>		
		420	<sup>3</sup> T <sub>2g</sub> (P)← <sup>3</sup> A <sub>2g</sub>		
		1000	<sup>3</sup> T <sub>1g</sub> ← <sup>3</sup> A <sub>2g</sub>	-	-
4	NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	650; 780	<sup>3</sup> T <sub>2g</sub> (F)← <sup>3</sup> A <sub>2g</sub> <sup>1</sup> E <sub>g</sub> ← <sup>3</sup> A <sub>2g</sub>		
		400	<sup>3</sup> T <sub>2g</sub> (P)← <sup>3</sup> A <sub>2g</sub>		

These bands were assigned to a *d-d* transition expected for Cu(II) complex compounds in a distorted tetragonal octahedron with various degrees of axial distortion.<sup>7-10</sup>

The spectrum of the complex compounds **3** and **4**, (Table 2) is a simple spectrum characteristic for six-coordinate Ni(II) complexes involving three spin-allowed transitions. Their assignments are in agreement with the literature data.<sup>11</sup> The band (650 and 760 nm; 650 and 780 nm) appears as doublet. The structure of this band was explained either by the low symmetry coupling or as a spin-forbidden transition to the <sup>1</sup>E<sub>g</sub> level.<sup>11</sup>

**The EPR spectra** of the CuL<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> and CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> recorded at room temperature on polycrystalline sample present EPR signals characteristic of a monomeric species of Cu(II) with various degrees of axial distortion (Table 2). Thus, the EPR signal of the CuL<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> would be consistent with elongated tetragonal-octahedral stereochemistry (when lowest  $g > 2.04$ ), while the EPR spectra of the CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> would be consistent with compressed tetragonal- octahedral stereochemistry (when lowest  $g < 2.03$ ).<sup>7,8</sup>

**IR spectra.** The positions of some infrared absorption bands within 400-4000 cm<sup>-1</sup> range of the complex compounds, free ligand and the pyrazole are listed in Table 3. The IR spectrum of the free ligand suggests that it is in a dimer form (Scheme 1). It presents a broad band in the 3500-3000 cm<sup>-1</sup> range centered at 3404 cm<sup>-1</sup>, due to  $\nu_{\text{OH}}$  associated and no band due to  $\nu_{\text{OH}}$  non-associated near 3600 cm<sup>-1</sup>. This might be explained through the involvement of the -COOH groups in inter- and intramolecular hydrogen bonds. The spectrum presents also two bands at 1708 cm<sup>-1</sup> and 1626 cm<sup>-1</sup>. The strong sharp band at 1626 cm<sup>-1</sup> is only consistent with the -COOH group involved in a dimer structure through intermolecular hydrogen bonds.<sup>12</sup> This structure is supported by the band due to  $\nu_{\text{C=O}}\delta_{\text{OH}}$  coupling (1266 cm<sup>-1</sup>). Upon coordination only the bands due to  $\nu_{\text{C=O}}$ ,  $\nu_{\text{OH}}$  assoc. and pyrazole ring are changed.

Table 3

The main absorption bands and their assignments in IR spectra (cm<sup>-1</sup>)

Nr. cr.	Ligand/ Compound	$\nu_{\text{OH}}$ non-assoc.	$\nu_{\text{OH}}$ assoc.	$\nu_{\text{C=O}}$ monomer	Pz stretching ring			
	<b>L</b>	-	3404w	1704m	1534vs	1488vs	1423sh	1383w
1	CuL <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub>	3650vw	3354w	1694m	1541ws	1493s	1430m	1395s
2	NiL <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub>	3650vw	3321w	1699m	1546vs	1498s	1420sh	1395s
3	ZnL <sub>2</sub> (CH <sub>3</sub> OH) <sub>2</sub>	3640vw	3393w	1701m	1549vs	1491s	1420sh	1393m
4	CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	-	3425m	1712m	1554vs	1494s	1399m	1343m
5	NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3650vw	3432w	1735w	1578vs	1545vs	1461m	1395w
6	ZnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	-	3410w	1725w	1577vs	1544vs	1460m	1393w
	<b>Pz</b>	-	-	-	1523m	1485s	1385s	1345s

for the ligand:  $\nu_{\text{C=O}}$  dimer = 1626s;  $\nu_{\text{C=O}}\delta_{\text{OH}}$  = 1266s

vs – very strong; s – strong; m – medium; w – weak; vw – very weak; br – broad; sh – shoulder

The bands due to  $\nu_{C=O}$  ( $1626\text{ cm}^{-1}$ ) and  $\nu_{C=O} + \delta_{OH}$  ( $1266\text{ cm}^{-1}$ ) disappear suggesting the breaking of the dimer structure. The bands due to  $\nu_{C=O}$  ( $1704\text{ cm}^{-1}$ ) and due to  $\nu_{OH}$  associated ( $3404\text{ cm}^{-1}$ ) are shifted to lower values for  $ML_2(CH_3OH)_2$  compounds but to higher ones for  $ML_2(H_2O)_2$  compounds. These changes could suggest that through metal complex formation the structure  $(-OH\dots N)$  disappears, while the structure  $(-OM\dots N)$  appears, suggesting the involvement of at least one  $-COOH$  group and the pyrazole ring upon the coordination to the metallic ion.

The bands assigned to pyrazole stretching ring are shifted to higher values generally. This would be consistent with the coordination of the pyrazole ring.<sup>13,14</sup>

IR spectrum of some compounds only shows a sharp band due to  $\nu_{OH}$  non-associated (near  $3640\text{ cm}^{-1}$ ) which could be a proof of the uncoordinated  $-COOH$  group. The IR spectra suggest the coordination of the ligand through N and O donor atoms. The ligand act bidentately through deprotonation of at least one  $-COOH$  group and via the lone pair of pyridine N of the pyrazole ring.

The six coordination surrounding the M(II) ion could be achieved by nitrogen and oxygen atoms in a plane and by axial coordination of methanol (water) molecules (Fig. 1).

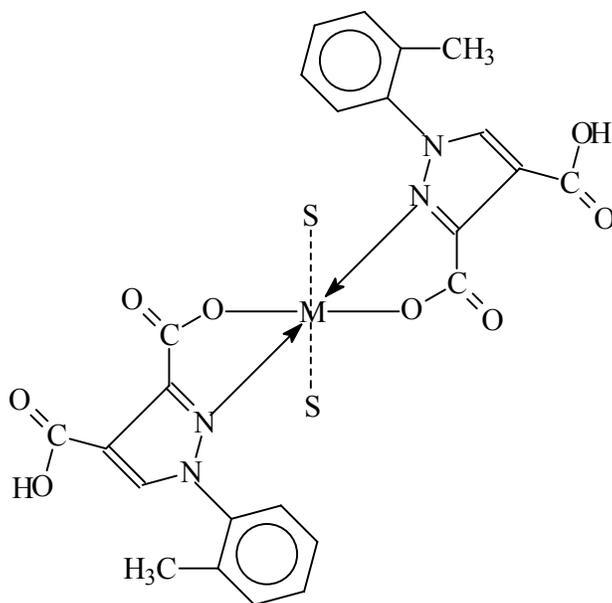


Fig. 1 – Structural formula proposed for the  $ML_2S_2$  compounds where: S =  $CH_3OH$  or  $H_2O$ ;

## EXPERIMENTAL

The carbon and hydrogen contents were determined by micro-combustion.

Analytical results for M, C, H were within  $\pm 0,4\%$  calculated values for the synthesised compounds.

The metal content was determined gravimetrically using the standard method.

The methanol content were calculated from the TG curve.

All melting points were recorded with a Boetius apparatus and are uncorrected.

Electronic spectra within 400-4000 nm range were obtained with VSU-2P Zeiss-Jena Spectrophotometer, using  $MgO$  as a standard.

IR spectra (KBr, pellets) were measured on a BIO-RAD FTS-135 Spectrometer.

EPR spectra were recorded at room temperature in polycrystalline powders on ART-5-IFA Spectrograph. The clystron frequency was 9060 MHz. The EPR spectral parameters were calculated against a Mn (II) standard.

Thermogravimetric analysis was carried out with a Paulik-Paulik-Erdey Derivatograph Q-1500 D MOM. Conditions of measurements: temperature range at  $1000\text{ }^\circ\text{C}$ ; heating program 10 degrees/min.; sensitivity DTA = 1/10; S = 50 mg;  $m_2 = 0.0418\text{ g}$ ;  $m_3 = 0.0449\text{ g}$ ; atmosphere over sample air.

NMR spectra were recorded on a Varian Gemini 300 Spectrometer operating at 300 MHz ( $^1\text{H-NMR}$ ) and 75 MHz ( $^{13}\text{C-NMR}$ ) respectively, in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ . The chemical shifts were referred to tetramethylsilane (TMS) as the internal standard.

5 Mmoles of ester was heated under reflux, under continuous stirring for 5 hours, with 10 % sodium hydroxide solution (30mL) and 5 mL ethanol. After cooling, the reaction mixture was acidified with concentrated HCl, the precipitate was filtered, washed with water and air dried. Recrystallization from a mixture of ethylacetate and acetonitril afforded white m.p. 209-212 $^{\circ}\text{C}$ .

Chemical analysis and  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra for the ligand:

1-(2-Methyl-phenyl)-pyrazole-3,4-dicarboxylic acid (L)

For  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_4$ , Found % C 58.87, H 4.42, N, 11.42; requires % C 58.54, H 4.09, N, 11.38.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ +TFA): 2.22 (s, 3 H, Me); 7.32-7.43 (m, 3 H, H-3', H-4', H-6'); 7.48-7.54 (m, 2 H, H-5'); 8.44 (s, 1 H, H-5);

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ +TFA): 16.9 (Me); 115.0 (C-4); 125.8, 127.3 (C-5', C-6'); 131.2, 131.8 (C-3', C-4'); 133.6 (C-2'); 136.8 (C-1'); 139.5 (C-5); 141.3 (C-3); 165.2, 167.4 (2 CO).

The metal acetates used were p.a. Merck grade.

The chelates,  $\text{ML}_2\text{S}_2$  (where S =  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ) have obtained following the same general procedure. In a typical experiment to a methanolic (aqueous) solution of ligand (2 mmoles) was added a methanolic (aqueous) solution of the metal acetate (1 mmole). The precipitate obtained was filtered off, washed with methanol (water) and air dried at room temperature.

Chemical analysis for the complex compounds:

$\text{ML}_2(\text{CH}_3\text{OH})_2$

1.  $\text{CuC}_{26}\text{H}_{28}\text{N}_4\text{O}_{10}$  Found %: Cu, 10.32; C, 50.58; H, 4.31; Requires %: Cu, 10.25; C, 50.36; H, 4.55.
2.  $\text{NiC}_{26}\text{H}_{28}\text{N}_4\text{O}_{10}$  Found %: Ni, 9.88; C, 50.39; H, 4.19; Requires %: Ni, 9.54; C, 50.76; H, 4.59.
3.  $\text{ZnC}_{26}\text{H}_{28}\text{N}_4\text{O}_{10}$  Found %: Zn, 10.69; C, 50.48; H, 4.35; Requires %: Zn, 10.51; C, 50.21; H, 4.54.

$\text{ML}_2(\text{H}_2\text{O})_2$

4.  $\text{CuC}_{24}\text{H}_{24}\text{N}_4\text{O}_{10}$  Found %: Cu, 11.01; C, 48.79; H, 4.10; Requires %: Cu, 10.73; C, 48.69; H, 4.09.
5.  $\text{NiC}_{24}\text{H}_{24}\text{N}_4\text{O}_{10}$  Found %: Ni, 9.91; C, 49.25; H, 4.22; Requires %: Ni, 9.99; C, 49.09; H, 4.12.
6.  $\text{ZnC}_{24}\text{H}_{24}\text{N}_4\text{O}_{10}$  Found %: Zn, 11.06; C, 48.69; H, 4.11; Requires %: Zn, 11.01; C, 48.54; H, 4.07.

## CONCLUSIONS

Upon coordination the dimer form of the ligand breaks.

The ligand acts bidentately via the pyridine nitrogen of the pyrazole ring and by the deprotonation of at least one  $-\text{COOH}$  group forming  $\text{ML}_2(\text{CH}_3\text{OH})_2$  or  $\text{ML}_2(\text{H}_2\text{O})_2$  compounds.

The other  $-\text{COOH}$  group is not involved in the coordination of the metal ion.

The nature of the metal ion and the medium reaction do not influence the type of compound.

The EPR spectra of the Cu(II) compounds suggest a elongated tetragonal-octahedral stereochemistry for the  $\text{CuL}_2(\text{CH}_3\text{OH})_2$  compound and a compressed tetragonal-octahedral stereochemistry for the  $\text{CuL}_2(\text{H}_2\text{O})_2$ .

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