

## Coordination compounds of Cu(II) with some substituted 2-(3,5-dimethyl-pyrazol-1-yl)-methyl-acetanilides as ligands

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**Abstract:** New complexes of Cu(II) with some substituted 2-(3,5-dimethyl-pyrazol-1-yl)-methyl-acetanilides (L) have been synthesized. The complex compounds,  $\text{CuL}_4\text{X}_2$  (where  $\text{X}^- = \text{Cl}, \text{Br}, \text{CH}_3\text{COO}$ ) were characterized by elemental analysis, as well as IR, UV-VIS, EPR spectroscopy. The study evidenced the influence of the position of the methyl group on the benzene ring and also of the anions on the physical properties of the compounds.

**Keywords:** pyrazol-1-yl-acetanilides, Cu(II) coordination compounds.

### INTRODUCTION

Previous papers reported the synthesis and characterization of some substituted 2-(3,5-dimethyl-pyrazol-1-yl)-methyl-acetanilides. It was shown that the nature, the position and the number of R substituents on benzene ring caused differences in the physical, chemical and pharmacological behaviour of the compounds.<sup>1–5</sup>

It seemed desirable to investigate whether or not, the nature, number and position of the substituents would also influence the coordination ability of these substituted acetanilides.

In this paper, the preparation and physical-chemical characterization of some Cu(II) complex compounds using as ligands three new substituted 2-(3,5-dimethyl-pyrazol-1-yl)-methyl-acetanilides (Fig. 1) are reported, in order to follow the coordination ability of these ligands and the influence of the position of the R– substituent of the anion on the complex type and their physical and chemical behaviour.

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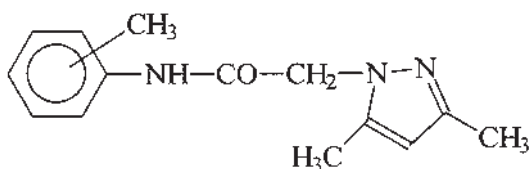


Fig. 1. Structural formula of the 2-(3,5-dimethyl-pyrazol-1-yl)-methyl-acetanilides. -CH<sub>3</sub> group = *ortho*, *meta*, *para*.

### EXPERIMENTAL

The ligands were synthesized<sup>1</sup> as previously described CuCl<sub>2</sub>·2H<sub>2</sub>O, CuBr<sub>2</sub> and Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O p.a. Merck were used.

**Synthesis.** The complex compounds were obtained following the same general procedure. In a typical experiment, to a warm methanolic solution (≈ 40 °C) of the ligand (4 mmol) was added a warm methanolic solution (≈ 40 °C) of Cu(II) salt (1 mmol). To the obtained green colored solution, 5 mL water were added, whereby a differently coloured powder product was immediately obtained. This was filtered off, washed with water and air dried at room temperature.

**Characterization.** The copper, chlorine and bromine contents in the complex compounds were determined by gravimetric analysis. The carbon and hydrogen contents were determined by microcombustion.

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

Electronic spectra within 380–900 nm range were obtained with a Jasco 570 V spectrophotometry by the diffuse reflectance technique with MgO as the standard.

EPR Spectra were recorded at room temperature on polycrystalline powders using an Art-5-IFA spectrograph. The clystron frequency was 9060 MHz. The EPR spectral parameters were calculated against a Mn(II) standard.

IR Spectra (KBr pellets) within the 400–4000 cm<sup>-1</sup> range in KBr pellets were performed on a BIO-RAD-FTS-135 spectrometer.

### RESULTS AND DISCUSSION

The synthesis was performed in a methanolic medium in a mole ratio Cu:L = 1:4, by interaction of a methanolic ligand solution with a methanolic solution of the Cu(II) salts. Nine new compounds of the CuL<sub>4</sub>X<sub>2</sub> type were obtained, where X<sup>-</sup> = Cl, Br, CH<sub>3</sub>COO and L = three ligands which differ in the position of methyl group on the benzene ring. All compounds were microcrystalline materials, differently colored and stable in air. They were characterized elemental analysis, as well as UV-VIS, IR and EPR spectroscopy.

#### *Chemical analysis:*

CuL<sub>4</sub>Cl<sub>2</sub>, Anal. calcd., for CuC<sub>56</sub>H<sub>68</sub>N<sub>12</sub>O<sub>4</sub>Cl<sub>2</sub>: Cu 5.73, C 60.72, H 6.19, Cl 16.40;

Found for Cu (*ortho* L)<sub>4</sub>Cl<sub>2</sub>: Cu 5.91, C 59.90, H 6.62, Cl 5.78;

Found for Cu (*meta* L)<sub>4</sub>Cl<sub>2</sub>: Cu 5.61, C 60.02, H 6.50, Cl 6.20;

Found for Cu (*para* L)<sub>4</sub>Cl<sub>2</sub>: Cu 5.71, C 60.47, H 6.42, Cl 6.80;

CuL<sub>4</sub>Br<sub>2</sub>, Anal. calcd. for CuC<sub>56</sub>H<sub>68</sub>N<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>: Cu 5.31, C 56.21, H 5.73, Br 13.36;

Found for Cu (*ortho* L)<sub>4</sub>Br<sub>2</sub>: CuC<sub>56</sub>H<sub>68</sub>N<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>: Cu 4.92, C 56.45, H 6.06, Br 12.98;

Found for Cu (*meta* L)<sub>4</sub>Br<sub>2</sub>: CuC<sub>56</sub>H<sub>68</sub>N<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>: Cu 5.20, C 55.98, H 6.09, Br 13.01;

Found for Cu (*para* L)<sub>4</sub>Br<sub>2</sub>: CuC<sub>56</sub>H<sub>68</sub>N<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>: Cu 5.50 C 56.30, H 6.11, Br 13.42;

$\text{CuL}_4(\text{CH}_3\text{COO})_2$ , Anal. calcd. for  $\text{CuC}_{60}\text{H}_{74}\text{N}_{12}\text{O}_8$ : Cu 5.50, C 62.40, H 6.46;  
 Found for Cu (*ortho* L) $_4(\text{CH}_3\text{COO})_2$ :  $\text{CuC}_{60}\text{H}_{74}\text{N}_{12}\text{O}_8$ : Cu 5.71, C 62.32, H 6.19;  
 Found for Cu (*meta* L) $_4(\text{CH}_3\text{COO})_2$ :  $\text{CuC}_{60}\text{H}_{74}\text{N}_{12}\text{O}_8$ : Cu 5.62, C 62.50, H 6.02;  
 Found for Cu (*para* L) $_4(\text{CH}_3\text{COO})_2$ :  $\text{CuC}_{60}\text{H}_{74}\text{N}_{12}\text{O}_8$ : Cu 5.48, C 62.45, H 6.80.

### Electronic spectra

Difuse reflectance electronic spectra of the complex compounds (Table I) are similar and they present one broad absorption band within the 642–866 nm range, differently centered, which is assigned to a  $d-d$  transition expected of Cu(II) complex compounds in a tetragonally distorted octahedron with various degrees of axial distortion.<sup>6–8</sup> The strong band within 338–374 nm range is assigned to the  $\pi-\pi^*$  transition characteristic of a substituted benzene ring; it is shifted depending on the position of the methyl group on the benzene ring and the nature of the anion.

TABLE I. Electronic spectra (nm) and physical data

Comp. -CH <sub>3</sub> group	CuL <sub>4</sub> Cl <sub>1</sub>			CuL <sub>4</sub> Br <sub>2</sub>			CuL <sub>4</sub> (CH <sub>3</sub> COO) <sub>2</sub>		
	$\lambda_{\text{max}}$	Colour	m.p./°C	$\lambda_{\text{max}}$	Colour	m.p./°C	$\lambda_{\text{max}}$	Colour	m. p./°C
<i>ortho</i>	350	light-green	118–120	368	dark-green	127–129	374	dark-green	99–100
	694			750			764		
<i>meta</i>	362	khaki	99–101	344	yellow-green	106–108	352	yellow-greenish	108–110
	676			748			750		
<i>para</i>	340	yellow-greenish	122–124	350	yellow-greenish	106–108	338	green	124–126
	642			746			704		
				866 sh					

sh = shoulder; m.p. °C of the ligand: *ortho*-L = 151–152; *meta*-L = 136–138; *para*-L = 145–147

### EPR Spectra

The EPR spectra recorded at room temperature of polycrystalline samples present EPR signals characteristic of a monomeric species of a Cu(II) ion (Table II). Some complexes present axial spectra with various degrees of axial distortion. It is known that, depending on the value of the lowest  $g$ -factor, these axial spectra are consistent with elongated tetragonal octahedral up to square coplanar stereochemistry (when the lowest  $g > 2.04$ ) or compressed tetragonal octahedral stereochemistry (when the lowest  $g < 2.03$ ).<sup>6–8</sup> Thus, the EPR spectra of all three complexes of the  $\text{CuL}_4\text{Br}_2$  type, the  $\text{CuL}_4\text{Cl}_2$  compound with the methyl group substituted in the *para* position and the  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  compounds with methyl group in the *meta* or *para* position present an EPR signal with two  $g$ -factors, which is consistent with elongated tetragonal octahedral geometry with  $g_{\parallel}/g_{\perp}$ . The EPR signal of the  $\text{CuL}_4\text{Cl}_2$  compounds with the methyl group substituted in the *ortho* or *meta* position and of the  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  compound with the methyl group in the

*ortho* position presents a third order anisotropy for the  $g$ -factor. Such a spectrum, depending on the value of the lowest  $g$ -factor, would be consistent with an elongated rhombic octahedral geometry, as in the  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  compound (when the lowest  $g > 2.04$ ) or a compressed rhombic geometry, as in both  $\text{CuL}_4\text{Cl}_2$  compounds (when the lowest  $g < 2.03$ ).

TABLE II. EPR Spectral parameters and the nuclear hyperfine splitting, A (mT)

Compd. -CH <sub>3</sub> group	CuL <sub>4</sub> Cl <sub>2</sub>			CuL <sub>4</sub> Br <sub>2</sub>		CuL <sub>4</sub> (CH <sub>3</sub> COO) <sub>2</sub>		
	$g_1$	$g_2 = g_{\perp}$	$g_3 = g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	$g_1$	$g_2 = g_{\perp}$	$g_3 = g_{\parallel}$
	–	A <sub>⊥</sub>	A <sub>∥</sub>	A <sub>⊥</sub>	A <sub>∥</sub>	–	A <sub>⊥</sub>	A <sub>∥</sub>
<i>ortho</i>	2.349	2.0847	2.0030	2.1318	2.2575	2.2522	2.1921	2.0491
	–	–	11.6	–	–	–	–	–
<i>meta</i>	2.2912	2.0795	2.0139	2.0384	2.2494	–	2.0415	2.2822
	–	–	16.0	2.72	14.51	–	2.74	19.9
<i>para</i>	–	2.1083	2.2559	2.1159	2.3069	–	2.0787	2.3005
	–	–	–	–	–	–	–	13.2

### IR spectra

Table III shows the assignments of the main bands in the IR spectra of the free ligands and of the complex compounds. For control of the assignments, the main bands of free pyrazole and 3,5-dimethyl-pyrazole,<sup>9–16</sup> are also given.

TABLE III. IR Spectra and assignments of the main bands (cm<sup>-1</sup>)

No	Ligand/Comp	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\delta_{\text{N-H}+\nu_{\text{C-N}}}$	Pz-ring stretching	Pz-bending
	<i>ortho-L</i>	3254s	1663vs	1587w	1549s, 1497vw, 1371vw, 1317vw	1036w, 972w
1	CuL <sub>4</sub> Cl <sub>2</sub>	3261m	1667vs	1588m	1538s, 1451m, 1370w, 1290w	1038w, 966w
2	CuL <sub>4</sub> Br <sub>2</sub>	3262m	1666s	1588m	1538s, 1459m, 1370w, 1290w	1040w, 966w
3	CuL <sub>4</sub> (Ac) <sub>2</sub>	3262s	1667vs	1588w	1538s, 1459m, 1370w, 1289w	1039w, 966w
	<i>meta-L</i>	*	1687vs	1623s	1571s, 1490m, 1389w, 1314m	1035w, 955w
4	CuL <sub>4</sub> Cl <sub>2</sub>	*	1683vs	1617s	1556m, 1491m, 1426w, 1312w	1037w, 954w
5	CuL <sub>4</sub> Br <sub>2</sub>	*	1683vs	1613s	1559vs, 1486s, 1428m, 1308m	1036w, 868w
6	cuL <sub>4</sub> (Ac) <sub>2</sub>	*	1683vs	1617s	1563s, 1491s, 1382w, 1314m	1036w, 868w
	<i>para-L</i>	*	1687vs	1069m	1543s, 1457s, 1410w, 1319w	1034vw, 978w
7	CuL <sub>4</sub> Cl <sub>2</sub>	*	1661vs	1610m	1544s, 1488s, 1410w, 1308w	1034vw, 961w
8	CuL <sub>4</sub> Br <sub>2</sub>	*	1661vs	1609m	1544s, 1409m, 1409m, 1308m	1037vw, 962w
9	CuL <sub>4</sub> (Ac) <sub>2</sub>	*	1683vs	1610vs	1516s, 1428m, 1428m, 1308m	1038vw, 961vw
	pz	*	–	–	1525m, 1485s, 1385s, 1345s	938s, 926m, 918m
	3,5-diMe-pz	*	–	–	1538m, 1474s, 1306s, 1315s	998sh, 825br

\*3600–2900 br; m; Ac = CH<sub>3</sub>COO<sup>-</sup>

The IR spectra of the free ligands reflect their molecular structure. The band due to the stretching frequency,  $\nu_{\text{N-H}}$ , appears as strong sharp band (3254 cm<sup>-1</sup>) for the

ligand with the methyl group in the *ortho* position, but as a broad band (3600–3000  $\text{cm}^{-1}$ ) split in five peaks for the ligands with the methyl group in *meta* (3515, 3484, 3278, 3210, 3090  $\text{cm}^{-1}$ ) and *para* (3415, 3296, 3263, 3189, 3116  $\text{cm}^{-1}$ ) position. The very strong amide band I,  $\nu_{\text{C=O}}$ , appears within the 1660–1693  $\text{cm}^{-1}$  range; the amide band II, due to the  $\delta_{\text{NH+CN}}$  coupling, is present within the 1587–1623  $\text{cm}^{-1}$ . These bands are little or not at all shifted in the IR spectra of the complex compounds. The bands due to the pyrazole ring stretching and pyrazole ring bending appear within the 1587–1314  $\text{cm}^{-1}$  range, and the 1024–1036  $\text{cm}^{-1}$  and 955–978  $\text{cm}^{-1}$ , respectively. Only these bands are markedly different from those of the free ligands. Some remarks concerning these bands should be made:

- the pyrazole ring stretching band  $\nu$  (1549, 1571, 1543  $\text{cm}^{-1}$ , respectively) is shifted to lower values in the IR spectra of the complex compounds with the methyl group in the *ortho* and *meta* position on the benzene ring;
- the very weak or medium band (1497, 1490, 1457  $\text{cm}^{-1}$ , respectively) is irregularly shifted;
- the band very weak or medium  $\nu$  (1371, 1389, 1362  $\text{cm}^{-1}$ , respectively) is shifted to higher values or is not shifted;
- the band (1317, 1314, 1319  $\text{cm}^{-1}$ ), respectively is shifted to lower values more much for the compounds of the ligands with methyl groups in *ortho* and *para* position;
- the band due to pyrazole ring bending  $\nu$  (1036, 1035, 1024  $\text{cm}^{-1}$ , respectively), is a little shifted to higher values while the band  $\nu$  (972, 955, 978  $\text{cm}^{-1}$ , respectively), is shifted to lower values;
- the assignments of the bands due to  $\nu_{\text{COOH}}$  (1575  $\text{cm}^{-1}$  asym. and 1425  $\text{cm}^{-1}$  sym) of the acetate ion is not possible, because of their overlapping with other bands in this range.

This coordination behavior of the ligands could suggest their coordination with Cu(II) ion *via* the lone pair of the pyridine nitrogen in pyrazole ring in a plane, acting monodentately. The six-coordinating surrounding the Cu(II) ion could be

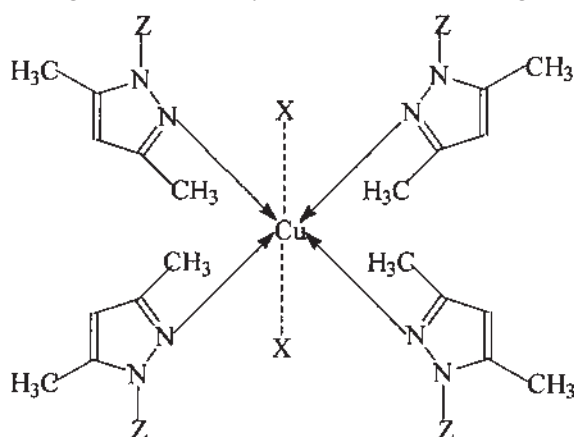


Fig. 2. Suggested structural formula for  $\text{CuL}_4\text{X}_2$  compounds type.  
 $\text{Z} = -\text{CH}_2\text{CONHC}_6\text{H}_4-\text{CH}_3$  (*o,m,p*)  $\text{X}^- = \text{Cl, Br, CH}_3\text{COO}$ .

achieved by the longer bonds to axial halide or acetate ions as in a distorted elongated geometry for some compounds, or by shorter bonds to axial chloride ion in a distorted compressed rhombic geometry or by longer bonds to axial acetate ion in a distorted elongated rhombic geometry. This is supported by their EPR and a electronic spectra (Fig. 2).

#### CONCLUSION

The three ligands act monodentately *via* the lone pair of the pyridine nitrogen in the pyrazole ring. The influence of both the position of the methyl group on the benzene ring and the anions is reflected in their physical properties and spectral data. These suggested a six-coordination surrounding for some compounds, the Cu (II) ion in an elongated tetragonal octahedral geometry for some compounds, or a compressed or elongated rhombic octahedral geometry for others.

These differences can be explained by electronic and steric effects of the methyl substituent and of the anions.

#### ИЗВОД

#### КООРДИНАЦИОНА ЈЕДИЊЕЊА Cu(II) СА НЕКИМ СУПСТИТУИСАНИМ 2-(3,5-ДИМЕТИЛ-ПИРАЗОЛ-1-ИЛ)-МЕТИЛ-АЦЕТАНИЛИДИМА КАО ЛИГАНДИМА

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Синтетисани су нови комплекси Cu(II) са неким супституисаним 2-(3,5-диметил-пиразол-1-ил)-метил-ацетанилидима (L). Комплексна једињења, CuL<sub>4</sub>X<sub>2</sub> (где је X = Cl, Br, CH<sub>3</sub>COO) су окарактерисана елементалном анализом, ИС, UV-VIS, EPR спектрима. Проучавање је указало на утицај положаја метил групе на бензеновом прстену као и анјона на физичке особине једињења.

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