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

CHRISTINA ZALARU*, MIRCEA IOVU, FLORICA ZALARU, AURELIA MEGHEA, MARIANA GIURGINCA and MARIA PLA VETI

*University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, 99-92 Pandurilor Road Bucharest, bUniversity of Medicine and Pharmaceutical "Carol Davila", Department of Organic Chemistry, 6 Traian V. Soares St. Bucharest, cUniversity of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 23 Dumbrava, Rosie St., Bucharest, dPolytechnic University, Industrial Faculty, 1 Polizu St., Bucharest, and eInstitute of Organic Chemistry "C.D. Nenitescu", Romanian Academy, Spl. Independentei 202B, Bucharest, Romania (e-mail: chmzalaru@yahoo.com)

(Received 3 November 2005, revised 14 May 2006)

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, CuL2X2 (where X = Cl, Br, CH3COO) 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.1–5

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 on the complex type and their physical and chemical behaviour.

* Corresponding author.

doi: 10.2298/JSC0703251Z
EXPERIMENTAL

The ligands were synthesized as previously described CuCl₂·2H₂O, CuBr₂ and Cu(CH₃COO)₂·H₂O 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 colored 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⁻¹ 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 CuL₄X₂ type were obtained, where X⁻ = Cl, Br, CH₃COO 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:

CuL₄Cl₂, Anal. calcd., for CuC₅₆H₆₈N₁₂O₄Cl₂: Cu 5.73, C 60.72, H 6.19, Cl 16.40;
Found for Cu (ortho L)₄Cl₂: Cu 5.91, C 59.90, H 6.62, Cl 5.78;
Found for Cu (meta L)₄Cl₂: Cu 5.61, C 60.02, H 6.50, Cl 6.20;
Found for Cu (para L)₄Cl₂: Cu 5.71, C 60.47, H 6.42, Cl 6.80;
CuL₄Br₂, Anal. calcd. for CuC₅₆H₆₈N₁₂O₄Br₂: Cu 5.31, C 56.21, H 5.73, Br 13.36;
Found for Cu (ortho L)₄Br₂: CuC₅₆H₆₈N₁₂O₄Br₂: Cu 4.92, C 56.45, H 6.06, Br 12.98;
Found for Cu (meta L)₄Br₂: CuC₅₆H₆₈N₁₂O₄Br₂: Cu 5.20, C 55.98, H 6.09, Br 13.01;
Found for Cu (para L)₄Br₂: CuC₅₆H₆₈N₁₂O₄Br₂: Cu 5.50 C 56.30, H 6.11, Br 13.42;
CuL₄(CH₃COO)₂, Anal. calcd. for CuC₆₀H₇₄N₁₂O₈: Cu 5.50, C 62.40, H 6.46;
Found for Cu (ortho L)₄(CH₃COO)₂: CuC₆₀H₇₄N₁₂O₈: Cu 5.71, C 62.32, H 6.19;
Found for Cu (meta L)₄(CH₃COO)₂: CuC₆₀H₇₄N₁₂O₈: Cu 5.62, C 62.50, H 6.02;
Found for Cu (para L)₄(CH₃COO)₂: CuC₆₀H₇₄N₁₂O₈: Cu 5.48, C 62.45, H 6.80.

Electronic spectra

Diffuse 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 ax-i-al distortion.⁶–⁸ The strong band within 338–374 nm range is assigned to the π–π* 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>
<thead>
<tr>
<th>Comp.</th>
<th>CuL₄Cl₂</th>
<th>CuL₄Br₂</th>
<th>CuL₄(CH₃COO)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
<td>368</td>
<td>374</td>
<td>374</td>
</tr>
<tr>
<td>642</td>
<td>750</td>
<td>368</td>
<td>374</td>
</tr>
<tr>
<td>meta</td>
<td>344</td>
<td>352</td>
<td>352</td>
</tr>
<tr>
<td>676</td>
<td>748</td>
<td>344</td>
<td>352</td>
</tr>
<tr>
<td>para</td>
<td>350</td>
<td>338</td>
<td>338</td>
</tr>
<tr>
<td>642</td>
<td>746</td>
<td>350</td>
<td>338</td>
</tr>
</tbody>
</table>


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 stereo-chemistry (when the lowest g > 2.04) or compressed tetragonal octahedral stereo-chemistry (when the lowest g < 2.03).⁶–⁸ Thus, the EPR spectra of all three complexes of the Cu L₄Br₂ type, the CuL₄Cl₂ compound with the methyl group substituted in the para position and the CuL₄(CH₃COO)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∥/g⊥. The EPR signal of the CuL₄Cl₂ compounds with the methyl group substituted in the ortho or meta position and of the CuL₄(CH₃COO)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 CuL₄(CH₃COO)₂ compound (when the lowest $g > 2.04$) or a compressed rhombic geometry, as in both CuL₄Cl₂ compounds (when the lowest $g < 2.03$).

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

<table>
<thead>
<tr>
<th>Compd.</th>
<th>CuL₄Cl₂</th>
<th>CuL₄Br₂</th>
<th>CuL₄(CH₃COO)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>–CH₃ group</td>
<td>$g_1$</td>
<td>$g_2 = g_\perp$</td>
<td>$g_3 = g_{</td>
</tr>
<tr>
<td>ortho</td>
<td>2.349</td>
<td>2.0847</td>
<td>2.0030</td>
</tr>
<tr>
<td>meta</td>
<td>2.912</td>
<td>2.0795</td>
<td>2.0139</td>
</tr>
<tr>
<td>para</td>
<td>–</td>
<td>2.1083</td>
<td>2.2559</td>
</tr>
</tbody>
</table>

### 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,⁹–¹⁶ are also given.

### TABLE III. IR Spectra and assignments of the main bands (cm⁻¹)

<table>
<thead>
<tr>
<th>No</th>
<th>Ligand/Comp</th>
<th>$\nu_{\text{N-H}}$</th>
<th>$\nu_{\text{C=O}}$</th>
<th>$\delta_{\text{N-H}}^{\text{+}}$</th>
<th>$\nu_{\text{C-N}}$</th>
<th>Pz-ring stretching</th>
<th>Pz-bending</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ortho-L</td>
<td>3254s</td>
<td>1663vs</td>
<td>1587w</td>
<td>1549s, 1497w, 1371w, 1317w</td>
<td>1036w, 972w</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CuL₄Cl₂</td>
<td>3261m</td>
<td>1667vs</td>
<td>1588m</td>
<td>1538s, 1451m, 1370w, 1290w</td>
<td>1038w, 966w</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CuL₄Br₂</td>
<td>3262m</td>
<td>1666s</td>
<td>1588m</td>
<td>1538s, 1459m, 1370w, 1290w</td>
<td>1040w, 966w</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>meta-L</td>
<td>3262s</td>
<td>1667vs</td>
<td>1588w</td>
<td>1538s, 1459m, 1370w, 1289w</td>
<td>1039w, 966w</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CuL₄Cl₂</td>
<td></td>
<td>1687vs</td>
<td>1623w</td>
<td>1571w, 1490m, 1389w, 1314w</td>
<td>1035w, 955w</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CuL₄Br₂</td>
<td></td>
<td>1683vs</td>
<td>1617w</td>
<td>1556m, 1491m, 1426w, 1312w</td>
<td>1037w, 954w</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>cuL₄(Ac)₂</td>
<td></td>
<td>1683vs</td>
<td>1613s</td>
<td>1559vs, 1486s, 1428m, 1308m</td>
<td>1036w, 868w</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>meta-L</td>
<td></td>
<td>1687vs</td>
<td>1617w</td>
<td>1563s, 1491s, 1382w, 1314m</td>
<td>1036w, 868w</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CuL₄Cl₂</td>
<td></td>
<td>1681vs</td>
<td>1610m</td>
<td>1544s, 1488s, 1410w, 1308w</td>
<td>1034w, 961w</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CuL₄Br₂</td>
<td></td>
<td>1661vs</td>
<td>1609m</td>
<td>1544s, 1409m, 1409m, 1308m</td>
<td>1037w, 962w</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CuL₄(Ac)₂</td>
<td></td>
<td>1683vs</td>
<td>1610w</td>
<td>1516s, 1428m, 1428m, 1308m</td>
<td>1038w, 961w</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3,5-diMe-pz</td>
<td></td>
<td>1683vs</td>
<td>1610w</td>
<td>1538m, 1474s, 1306s, 1315s</td>
<td>998sh, 825br</td>
<td></td>
</tr>
</tbody>
</table>

*3600–2900 br; m; Ac = CH₃COO⁻

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⁻¹) for the
ligand with the methyl group in the ortho position, but as a broad band (3600–3000 cm⁻¹) split in five peaks for the ligands with the methyl group in meta (3515, 3484, 3278, 3210, 3090 cm⁻¹) and para (3415, 3296, 3263, 3189, 3116 cm⁻¹) position. The very strong amide band I, νC=O, appears within the 1660–1693 cm⁻¹ range; the amide band II, due to the δNH+CN coupling, is present within the 1587–1623 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 cm⁻¹ range, and the 1024–1036 cm⁻¹ and 955–978 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 ν (1549, 1571, 1543 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 cm⁻¹, respectively) is irregularly shifted;
– the band very weak or medium ν (1371, 1389, 1362 cm⁻¹, respectively) is shifted to higher values or is not shifted;
– the band (1317, 1314, 1319 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 ν (1036, 1035, 1024 cm⁻¹, respectively), is a little shifted to higher values while the band ν (972, 955, 978 cm⁻¹, respectively), is shifted to lower values;
– the assignments of the bands due to νCOOH (1575 cm⁻¹ asym. and 1425 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 Cu₄X₂ compounds type.](image-url)
achieved by the longer bands 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.

REFERENCES