

## TRANSITION METAL COMPLEXES WITH PYRAZOLE-BASED LIGANDS

### Part 12. Characterisation and thermal decomposition of $\text{CuCl}_2$ complexes with di- and trisubstituted pyrazoles

*K. Mészáros Szécsényi*<sup>1</sup>, *V. M. Leovac*<sup>1</sup>, *K. Jaćimović*<sup>2</sup>, *V. I. Češljević*<sup>1</sup>,  
*A. Kovács*<sup>3</sup> and *G. Pokol*<sup>4</sup>

<sup>1</sup>University of Novi Sad, Faculty of Sciences, Institute of Chemistry, 21000 Novi Sad,  
Trg D. Obradovića 3, Yugoslavia

<sup>2</sup>Faculty of Metallurgy and Technology, Podgorica, Yugoslavia

<sup>3</sup>Research Group for Technical Analytical Chemistry of the Hungarian Academy of Sciences at the  
Institute for General and Analytical Chemistry, Technical University of Budapest,  
H-1521 Budapest, Hungary

<sup>4</sup>Institute for General and Analytical Chemistry, Technical University of Budapest,  
H-1521 Budapest, Hungary

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#### Abstract

The synthesis of copper(II) chloride complexes with 3,5-dimethylpyrazole, 1-carboxamidine-3,5-dimethylpyrazole, 5-amino-4-carboxamide-1-phenylpyrazole and 4-acetyl-3-amino-5-methylpyrazole is described. The compounds are characterized by elemental analysis, FT-IR spectroscopy, thermal methods, magnetic moment and molar conductivity measurements. Thermal decomposition of the dichloro-(3,5-dimethylpyrazole)-copper(II) complex results in an unstable intermediate with a stoichiometric composition. The decomposition of the other compounds is continuous.

**Keywords:** 4-acetyl-3-amino-5-methylpyrazole, 5-amino-4-carboxamide-1-phenylpyrazole, 1-carboxamide-3,5-dimethylpyrazole, 1-carboxamidine-3,5-dimethylpyrazole, copper(II) complexes, 3,5-dimethylpyrazole, FT-IR spectroscopy, magnetic measurements, thermal decomposition

#### Introduction

Continuing our studies on transition metal complexes with pyrazole type ligands [1–5] we examined reactions between copper(II) chloride and 5-amino-4-carboxamide-1-phenylpyrazole, ( $\text{L}^2$ ), 1-carboxamide-3,5-dimethylpyrazole, ( $\text{HL}^3$ ), 1-carboxamidine-3,5-dimethylpyrazole, ( $\text{HL}^4$ ) and 4-acetyl-3-amino-5-methylpyrazole ( $\text{HL}^5$ ) ligands. Depending on the ligand type and/or the ligand-to-metal ratio mono- and bis(ligand) complexes are formed. In the reaction of 1-carboxamide-3,5-dimethylpyrazole, ( $\text{HL}^3$ ), with  $\text{CuCl}_2$ , a decarboxamidation of the ligand occurred resulting in mono- and bis(ligand)

copper(II) chloride complexes of 3,5-dimethylpyrazole ( $\text{HL}^1$ ). Complexes of the following compositions are obtained:  $[\text{CuCl}_2(\text{HL}^1)]_2$ ,  $\text{CuCl}_2(\text{HL}^1)_2$ ,  $\text{CuCl}_2(\text{L}^2)_2$ ,  $\text{CuCl}_2(\text{HL}^4)$  and  $\text{CuCl}_2(\text{HL}^5)_2$ .

Some physico-chemical properties of the compounds were determined. Special attention was paid to the relationship between the structural characteristics and thermal behaviour of the compounds. The thermal properties of the complexes are compared to the thermal data of similar pyrazole complexes with other cations.

## Experimental

All the pyrazole derivatives were commercial products of the Aldrich Company except of the 4-acetyl-3-amino-5-methylpyrazole, ( $\text{HL}^5$ ). The synthesis of this ligand has been described elsewhere [1].

The elemental, FT-IR and thermal analyses were performed using the standard methods and instrumentation described in [2]. In the case of the  $\text{CuCl}_2(\text{HL}^5)_2$  the decomposition was also followed by mass spectrometry (Balzers Termostar GSD 300 T, capillary MS).

Magnetic susceptibility measurements were conducted at room temperature using a magnetic susceptibility balance MSB-MKI, Sherwood Scientific Ltd., Cambridge. The data are corrected for diamagnetic susceptibilities.

## Results and discussion

All the complexes were prepared reacting hot ethanolic solutions of the appropriate ligand and copper(II) chloride dihydrate in a ligand-to-metal ratio of 2:1 except in reaction with  $\text{HL}^3$ , where a 1:1 ligand-to-metal ratio was also applied. The composition of the compounds and the elemental analyses data are given in Table 1. All the complexes are coloured and well soluble in DMF. Their solubility is lower in alcohols (MeOH, EtOH) and significantly lower in water. The effective magnetic moment of the complexes ( $1.8 > \mu_{\text{eff.}} > 1.9$ ) corresponds to monomeric  $d^9$  systems except of that of the  $[\text{CuCl}_2(\text{HL}^1)]_2$  complex. The lower magnetic moment for this compound ( $\mu_{\text{eff.}}=1.55$ ) suggests a dimeric structure [6]. This supposition is supported also with the compound's lower solubility according to the corresponding bis(ligand)complex. Low molar conductivity ( $\lambda_{(\text{DMF})} < 30$ ) is characteristic of all formed compounds referring to the co-ordination of the chlorine. Some physico-chemical properties of the compounds are presented in Table 2.

In all the compounds the copper(II) is tetraordinated with the chloride ions and the pyridine-type nitrogen of the pyrazole rings and in case of the  $\text{CuCl}_2(\text{HL}^4)$  complex with the imido nitrogen of the carboxamidine group. This kind of the co-ordination is proved by single crystal X-ray analysis of the compound [7].

$[\text{CuCl}_2(\text{HL}^1)]_2$  and  $\text{CuCl}_2(\text{HL}^1)_2$  were prepared reacting 1-carboxamide-3,5-dimethylpyrazole, ( $\text{HL}^3$ ), with copper(II) chloride in a ligand-to-metal ratio of 1:1 and 2:1, respectively. In this reaction an elimination of the carboxamide group from the

ligand takes place. Hence, instead of the expected  $\text{CuCl}_2(\text{HL}^3)_2$  compound complexes containing 3,5-dimethylpyrazole ( $\text{HL}^1$ ) moieties are formed. The loss of the carboxamide group during the reaction is proved by both the elemental analysis data and the missing  $\nu(\text{C}=\text{O})$  vibrational band at  $1720\text{ cm}^{-1}$  from the IR spectra of the products. Exclusively  $\text{CuCl}_2(\text{HL}^1)_2$  complexes (green crystals) were obtained when the ligand-to-metal ratio was 2:1, while a mixture of  $\text{CuCl}_2(\text{HL}^1)_2$  and  $[\text{CuCl}_2(\text{HL}^1)]_2$  (golden crystals) was found using a ratio of 1:1. The two complexes in the mixture can be separated using the good solubility of  $\text{CuCl}_2(\text{HL}^1)_2$  in ethanol.

**Table 1** Composition of the compounds and elemental analysis data

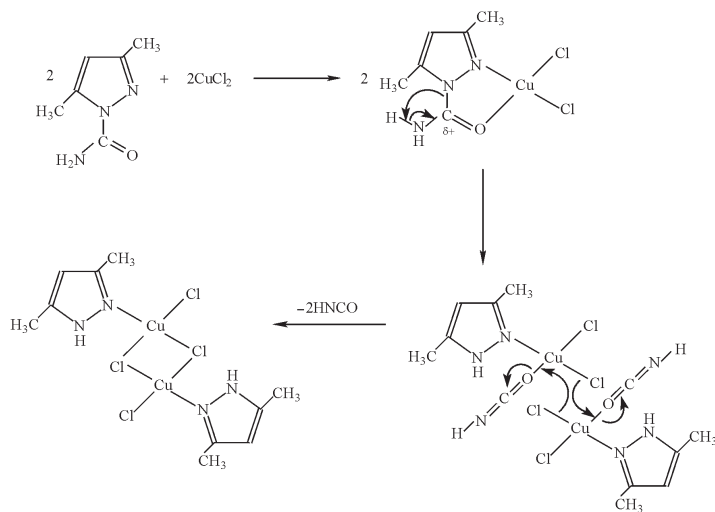
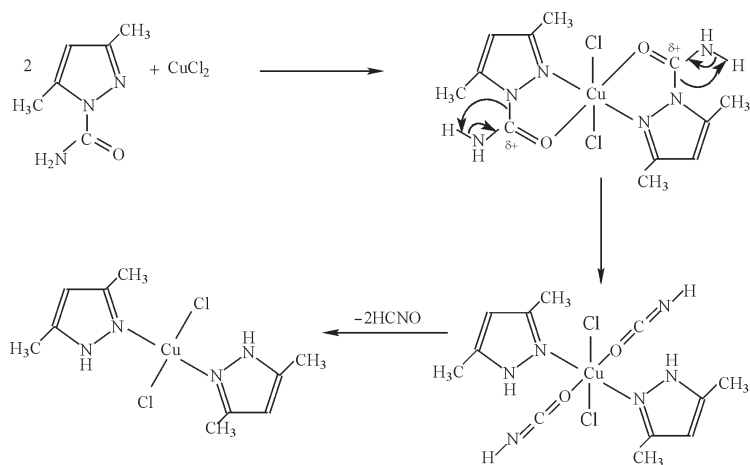
Compound	Found (Calculated)/%		
	C	H	N
1 $[\text{CuCl}_2(\text{HL}^1)]_2$	26.23 (26.04)	3.56 (3.50)	11.95 (12.15)
2 $\text{CuCl}_2(\text{HL}^1)_2$	37.18 (36.76)	5.02 (4.94)	17.10 (17.15)
3 $\text{CuCl}_2(\text{L}^2)_2$	44.42 (44.57)	4.38 (3.74)	20.29 (20.80)
4 $\text{CuCl}_2(\text{HL}^4)$	26.08 (26.43)	3.39 (3.70)	20.70 (20.55)
6 $\text{CuCl}_2(\text{HL}^5)_2$	35.46 (34.92)	4.81 (4.39)	20.82 (20.36)

**Table 2** Some physico-chemical properties of the complexes

Compound	Color	$\mu_{\text{eff.}}, \mu_{\text{B}}$	$\lambda_{\text{M}}(\text{DMF}),$ $\text{S}/\text{cm}^2\text{ mol}^{-1}$
1 $[\text{CuCl}_2(\text{HL}^1)]_2$	golden	1.55	28.3
2 $\text{CuCl}_2(\text{HL}^1)_2$	green	1.81	24.2
3 $\text{CuCl}_2(\text{L}^2)_2$	black	1.87	22.0
4 $\text{CuCl}_2(\text{HL}^4)$	blue	1.82	24.7
8 $\text{CuCl}_2(\text{HL}^5)_2$	black	1.81	23.4

A probable reaction mechanism of the complex formation of  $\text{CuCl}_2$  with  $\text{HL}^3$  resulting in  $[\text{CuCl}_2(\text{HL}^1)]_2$  and  $\text{CuCl}_2(\text{HL}^1)_2$  compounds is presented in Schemes 1 and 2, respectively. The first step is a (N, O) co-ordination of the ligand. This is accompanied by an increased polarisation of the  $\text{C}=\text{O}$  bond followed by a synchronous break of the  $\text{N}-\text{H}$  and  $\text{N}-\text{C}$  bonds and by the formation of an unstable isocyanic acid derivative. In the last step the better  $\text{Cl}^-$  nucleophile is remaining as a constituent of the compound giving  $[\text{CuCl}_2(\text{HL}^1)]_2$  or  $\text{CuCl}_2(\text{HL}^1)_2$  complexes, while the isocyanic acid is eliminated. The elimination is promoted by the solvent ethanol forming ethyl-carbamate. A decarboxamidation process was also observed in the reaction of cobalt(II) chloride [8] and zinc(II) chloride [9] with the same ligand, while with copper(II), nickel(II) and cobalt(II) perchlorates and cobalt(II) nitrate the expected bis( $\text{HL}^3$ ) complexes were formed [9].

Mono- and bis(ligand) complexes of copper(II) chloride with 3,5-dimethylpyrazole synthesised using 3,5-dimethylpyrazole ligand are already described in lit-



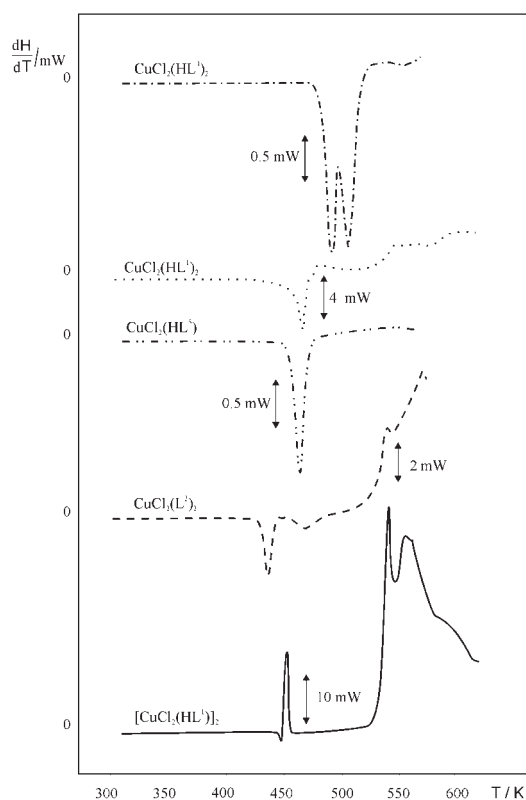
erature [6, 10]. However, their synthesis starting with 1-carboxamide-3,5-dimethylpyrazole is described for the first time. On the basis of ESR spectroscopy data and the strong antiferromagnetic ordering in the crystal for the mono(ligand) complex a dimeric quasi-octahedral structure may be proposed which is established through the bridging chloride atoms [6]. The structure of the bis(ligand)  $\text{CuCl}_2$  complex is proposed on the basis of the structure of an analogous bis( $\text{HL}^1$ ) zinc chloride complex,  $\text{ZnCl}_2(\text{HL}^1)_2$ , which was determined by X-ray analysis. For this compound a tetrahedral arrangement around  $\text{Zn}(\text{II})$  was found [11]. Based on the known similarity of Zn and Cu complexes and on the magnetic moment of  $\text{CuCl}_2(\text{HL}^1)_2$  ( $\mu_{\text{eff.}}=1.81$ ) we can assume a distorted tetrahedral structure for this compound.

In the reaction of the 5-amino-4-carboxamide-1-phenylpyrazole ( $L^2$ ) and  $\text{CuCl}_2$  a bis(ligand) complex is formed. It has been shown that with a bulky substituent on the pyrrolic nitrogen atom *trans*-square-planar complexes are obtained [12]. On this basis and on the basis of the value of the effective magnetic moment to the  $\text{CuCl}_2(L^2)_2$  complex a distorted *trans*-square-planar structure may be prescribed.

The X-ray analysis data refer to a square-planar geometry of the  $\text{CuCl}_2(\text{HL}^4)$  compound, also [7]. For the  $\text{CuCl}_2(\text{HL}^5)_2$  around copper(II) a very distorted tetrahedral environment was found by X-ray structure analysis [1].

#### *Thermal decomposition of the compounds*

The decomposition of the compounds starts with an endothermic process followed with an exothermic one (DSC curves, Fig. 1). The course of the decomposition up to 550 K does not depend on the gas carrier. The decomposition in argon atmosphere usually slows down and is not complete up to 1100 K. This is the case for compounds with  $\text{HL}^1$ ,  $L^2$  and  $\text{HL}^5$ , while the complex with  $\text{HL}^4$  decomposes completely in both atmospheres up to 950 K with the difference that in the air the decomposition is complete at 850 K.



**Fig. 1** DSC curves of the complexes

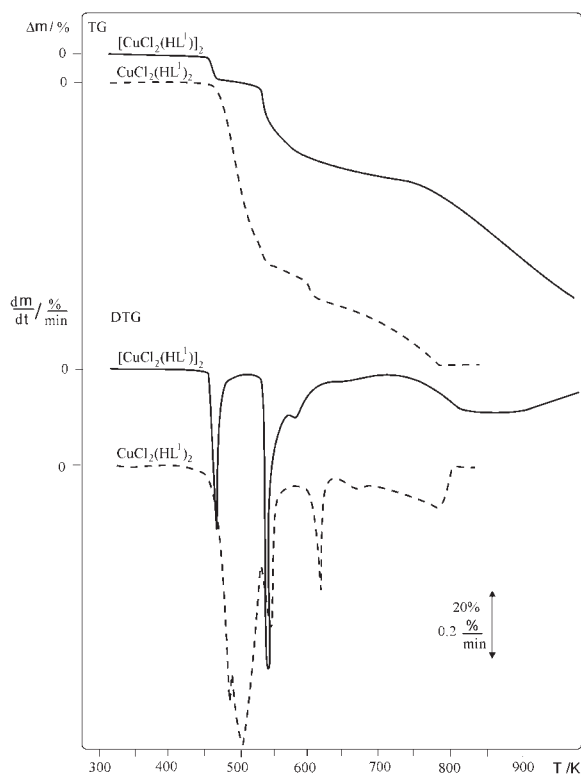
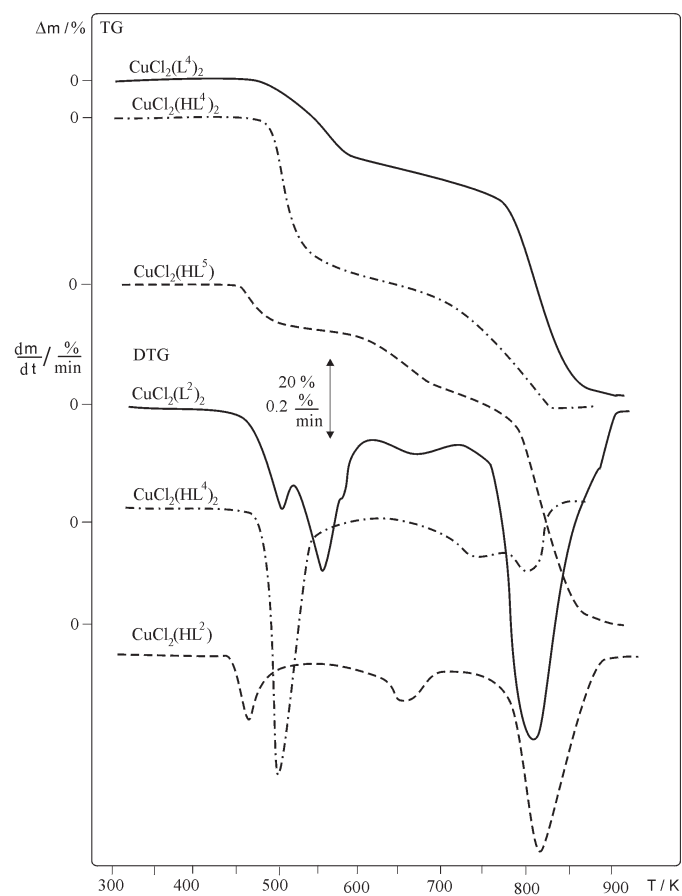


Fig. 2 TG and DTG curves of the complexes with  $\text{HL}^1$

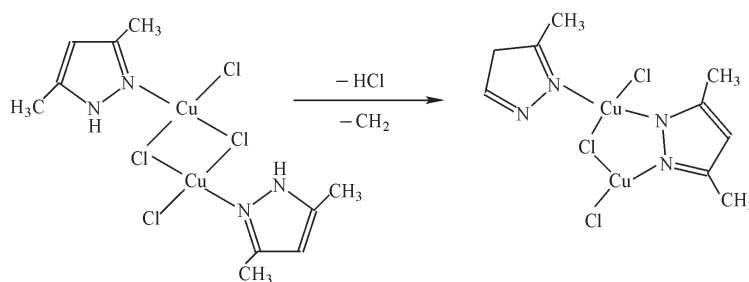
TG and DTG decomposition curves are presented in Figs 2 and 3. All the compounds begin to decompose in the temperature range of 450–480 K (Figs 1–3) which means that there is not a significant difference in their thermal stability at the beginning of the decomposition.

To the first decomposition step of the dimeric  $[\text{CuCl}_2(\text{HL}^1)]_2$  complex very sharp DTG and DSC peaks belong (Figs 1 and 2). The decomposition begins endothermally which is followed immediately with an exothermic process. At this stage a decomposition product with a stoichiometric composition is formed that decomposes almost immediately. By freezing-out technique the intermediate was isolated and investigated by IR spectroscopy. The most characteristic changes in the IR spectrum of the intermediate with respect to the starting compound are the disappearance of the  $\nu(\text{NH})$  stretching and  $\nu(=\text{CH})$  stretching bands as well as considerable alterations in the bands of the pyrazole ring vibrations. On the other hand, the characteristic bands of the methyl groups are unchanged. In spite of this fact, the EGA measurement indicates the departure of an organic fragment. Taking this in consideration, probably beside the departure of a HCl molecule a partial demethylation takes place, which was



**Fig. 3** TG and DTG curves of the complexes with  $L^2$ ,  $HL^4$  and  $HL^5$

observed earlier in pyrazole complexes with a methyl-group in position 5 [2]. This evidence, IR data and the mass loss (found: 11.0; calcd: 10.95%) suggest the decomposition mechanism which is presented in Scheme 3:



**Scheme 3**

The degradation of the dimeric  $[\text{CuCl}_2(\text{HL}^1)]_2$  complex in air is not complete up to 1000 K, while the bis(ligand) complex decomposes completely to CuO (found: 17, calcd: 19.45%).

The thermal stability of the  $\text{CuCl}_2(\text{L}^2)_2$  with a bulky aryl substituent on the pyrrolic nitrogen atom is somewhat less according to the other complexes. Its decomposition most likely begins with the breaking off of the aryl-groups (found: 25, calcd: 28.60%). The end product at 900 K in air atmosphere is probably copper(II) oxide with some coke residue.

The decomposition of the last two complexes is continuous. The  $\text{CuCl}_2(\text{HL}^4)$  decomposition probably begins with the demethylation and/or departure of the 3,5-dimethylpyrazole (found: 40, calcd: 35.26%) ligand. The end product is copper(II) oxide in both atmospheres (found: 28, calcd.: 29.18%).

The MS spectrum of the gaseous decomposition products at the beginning of the  $\text{CuCl}_2(\text{HL}^5)_2$  decomposition with 4-acetyl-3-amino-5-methylpyrazole ligand shows peaks for ammonia, methyl and methylen groups. Thus, in this case probably an NH-bridge formation takes place as was supposed at the decomposition of other pyrazole complexes with  $\text{NH}_2$ -group in position 3, together with a demethylation, characteristic of the 5-methyl derivatives of pyrazoles [2, 3]. The substituents are breaking off side by side. Above 700 K the pyrazole skeleton is destroying and a copper(II) oxide end product is obtained (found: 16.3, calcd: 19.30%).

## Conclusions

In reaction of the 1-carboxamide-3,5-dimethylpyrazole with copper(II) chloride a decarboxamidation takes place. Depending on the ligand-to-metal ion ratio a mono- or bis(3,5-dimethylpyrazole) complexes are formed.

The geometry of the compounds is determined primarily by the ligand. However, for the mono(ligand) complex with  $\text{HL}^1$  an octahedral geometry is prescribed, while for the bis(ligand) complex with the same ligand probably a tetrahedral structure is characteristic. A very distorted tetrahedral environment was found around copper(II) in  $\text{CuCl}_2(\text{HL}^5)_2$ .  $\text{CuCl}_2(\text{HL}^4)$  possess a square-planar geometry. A *trans*-square-planar geometry is prescribed to  $\text{CuCl}_2(\text{L}^2)_2$  complex.

The thermal decomposition pattern of the compounds is also different. The mono(ligand) complex with  $\text{HL}^1$  decomposes exothermally very rapidly to an unstable intermediate with a stoichiometric composition. The decomposition of the other compounds is continuous. However, on the basis of our experience with similar compounds [2, 5], the IR-spectrum of the intermediate and the MS spectral data we can state, that the decomposition most probably proceeds through a demethylation when there is a methyl-group in the position 5, *e.g.* in complexes with  $\text{HL}^4$  and  $\text{HL}^5$ . Additionally, in the case of the compound with the latter ligand at the first step likely an NH-bridge formation takes place parallelly with the demethylation as was observed in other complexes with a 3-amino-group [2, 5].



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