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TRANSITION METAL COMPLEXES WITH PYRAZOLE-BASED LIGANDS
Part 21. Thermal decomposition of copper and cobalt halide complexes with 3,5-dimethyl-1-thiocarboxamidepyrazole

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The thermal decomposition of $Cu_2L_2Cl_4$, $Cu_2L_2Cl_2$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$ complexes (**L**=3,5-dimethyl-1-thiocarboxamide-pyrazole) is described. The influence of the central ion to ligand mole ratio on the course of complex formation is examined in reaction of **L** with copper(II) chloride. In Cu(II):L mole ratio of 1:1, in methanolic solution the reaction yields to yellow-green $Cu_2L_2Cl_4$ crystals. In the filtrate a thermodynamically more stable orange $Cu_2L_2Cl_2$ copper(I) complex is forming. With a Cu(II):**L** mole ratio of 1:2 only the latter compound is obtained. The composition and the structure of the compounds have been determined on the basis of customary methods. On the basis of FTIR spectrum of the intermediate which is forming during the thermal decomposition of $Cu_2L_2Cl_2$ a decomposition mechanism is proposed.

Keywords: *cobalt(II) chloride or bromide complexes, copper(I) chloride or bromide complexes, copper(II) chloride or bromide complexes, coupled TG-MS measurement, 3,5-dimethyl-1-carboxamidepyrazole, TA*

Introduction

Pyrazole type complexes are extensively studied mainly because of their biological activity [1]. They are often used in modeling the active centers of enzymatic reactions [2, 3]. As these reactions take place at mild conditions and are usually very selective there are attempts to use them in chemical industry [4]. There are examples of use of pyrazole complexes as precursors in processing thin films by metal organic vapor deposition processes [5–7].

The aim of our systematic studies on pyrazole type complexes is to determine the most important factors governing the complex formation reaction and to examine how the structure affects the thermal stability of the compounds [8–11]. Namely, all potential practical applicability of new compounds claims not only on their thermal stability but also the understanding of the decomposition mechanism, often determined by coupled thermal and MS or FTIR techniques [12–18]. Besides, during the thermal decomposition stable compounds can be formed, offering thus a way to a solid phase synthesis of new compounds [19–21].

In this paper we report the synthesis, characterization and thermal decomposition of $Cu_2L_2Cl_2$ (**L**=3,5-dimethyl-1-thiocarboxamidepyrazole) together with thermal decomposition of $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$ complexes with the same ligand.

Experimental

All chemicals for synthesis were analytical reagent grade and used without any purification. Physico-chemical characterizations are conducted by usual methods and are described in details in [11].

Syntheses

The synthesis and the structure of the 3,5-dimethyl-1-thiocarboxamidepyrazole ligand, **L** [22] and the complexes of $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$ is described elsewhere [23].

$Cu_2L_2Cl_2$

Methanolic solutions of $CuCl_2{\cdot}2H_2O$ (1 mmol, 5 cm^3) and **L** (2 mmol, 5 cm^3) were mixed in a mole ratio of 1:2. The mixture was heated at 310 K (~40°C) under reflux for 1 h. The precipitation of orange microcrystalline $Cu_2L_2Cl_2$ ($Cu_2C_{12}H_{18}N_6S_2Cl_2$) began instantly. After 5 h the precipitate was filtered off,

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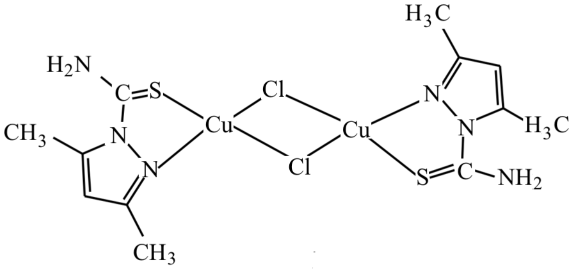
washed with cold methanol and air dried. Yield: 67.1%. Elemental analysis data Found, % (Calcd., %): C, 28.79 (28.35); H, 3.58 (3.57); N, 16.51 (16.53), Cu, 24.25 (25.00). FTIR-spectrum (cm^{-1}, KBr): 3276s, 3105s, 1628s, 1583s, 1153m, 873s. Molar conductivity of 10^{-3} mol dm^{-3} solution in DMF, λ_M(DMF), 39.6 S cm^2 mol^{-1}.

Results and discussion

The structure of $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$ has been determined by single crystal X-ray diffraction [23]. $Cu_2L_2Cl_4$ and $Co_2L_2Cl_4$ are isostructural. From the three potential donors of the ligand (the pyrazole ring pyridine N atom, the N and S atoms of the thiocarboxamide moiety) the coordination is established through the pyridine N atom of the pyrazole ring and S atom of the thiocarboxamide group forming neutral centrosymmetric units in which metal ions are doubly bridged by two chlorine atoms. In this way, metal atoms are sited in a distorted trigonal bipyramidal environment. In the bromide complex the coordinating atoms are the same. During the complex formation reduction of Cu(II) to Cu(I) occurs. The obtained $Cu_2L_2Br_2$ also has a centrosymmetric dimer structure with a distorted tetrahedral geometry around copper(I). However, instead of halide bridges, the two coppers are sulfur-bridged.

The FTIR spectrum of $Cu_2L_2Cl_2$ is very similar to those for the other three compounds. In all of the complexes the νCS vibration appears at lower frequency (873, 848, 870 and 842 cm^{-1} in $Cu_2L_2Cl_2$, $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$, respectively) than that in the ligand (880 cm^{-1}) suggesting a coordination through the sulfur atom in $Cu_2L_2Cl_2$, also. All attempts to prepare $Cu_2L_2Cl_2$ single crystals have failed. The similar composition of the copper(I) chloride and bromide compounds may refer to a similar structure for these two complexes. Powder X-ray diffraction patterns of $Cu_2L_2Cl_2$ suggest that it is most likely not isostructural with the corresponding bromo complex. However, neither the powder X-ray diffraction patterns nor the FTIR data are supporting or excluding that the two compounds are isosturctural. Beside the sulfur bridged copper atoms, it is possible that in the chlorine compound the copper centers are doubly bridged by chlorines instead of sulfur atoms, also with a distorted tetrahedral dimer structure (Scheme 1).



Scheme 1 Di-μ-chloro-bis{3,5-dimethyl-1-thiocarboxamide-copper(I)}

Factors determining the course of complex formation

One of the aims of our research work is to determine the most important factors that influence the complex formation. Some of these factors are as follows: the quality and position of the pyrazole substituents, the basicity of the components, the crystal field stabilization energy (CFSE), the steric requirement of the components, redox properties, the interaction of the components with the solvent, etc. In addition, ligands with groups like thiocarboxamide moiety may be deprotonated as a consequence of the Brønsted basicity of the anion [24] or by adding base to the reaction mixture [11]. Sometimes, even the CFSE is enough for the deprotonation of the ligand [25].

The copper complexes were synthesized in methanolic solution with a Cu(II):**L** mole ratio of 1:1. The Brønsted basicity of both the chloride and bromide ion in methanol is too low for the deprotonation of the thiocarboxamide group. In spite of similar experimental conditions, the structure of the chlorine and bromine compound is different. The coordinating atoms are the same (N, S), however, in the case of the bromide complex the reduction of Cu(II) to Cu(I) is taking place. This phenomenon may be explained by the lower standard redox potential of the $Br_2/2Br^-$ system compared to the $Cl_2/2Cl^-$ system. By reduction of Cu(II) to Cu(I) the borderline soft Cu(II) acid transforms to soft Cu(I) promoting the soft–soft interaction with soft sulfur and bromine bases in accordance with the Hard Soft Acid Base principle (HSAB, [26–28]). The formed compound is also sterically stabilized. Namely, as a consequence of the reduction, the molecule contains only one bromide per copper(I). This stabilization effect in the case of the corresponding copper(I) chloride complex is emphasized in forming a thermodynamically more stable Cu(I) compound from the filtrate after precipitating the kinetically favored Cu(II) complex. Namely, in the reaction of $CuCl_2\cdot 2H_2O$ and **L** in a mole ratio of 1:1 in methanolic solution two compounds are formed. Under kinetic control the yellow-green Cu(II)-complex, $Cu_2L_2Cl_4$, is crystallizing in form of single crystals. From the filtrate the thermodynamically more stable microcrystalline diamagnetic Cu(I)-complex, $Cu_2L_2Cl_2$ has been precipitated. When the Cu(II):**L** ratio is raised to 1:2 and at somewhat higher temperature (~40°C) the only product of the reaction is the thermodynamically stable $Cu_2L_2Cl_2$. The excess of the ligand probably promotes the reduction of Cu(II).

The role of the solvent and the anion in complex formation may be presented by the reaction of Co(II) acetate and sulfate with **L** in methanolic solution:in both cases the same pink colored cobalt(III) complex, Co(L–H)$_3$, was obtained [11]. In reaction of CoCl$_2$ and **L** under similar conditions no crystallization was observed. The deep blue color of the methanolic solution refers to a complex formation of different type than that observed with Co(Oac)$_2$ and CoSO$_4$. In acetone, instead of the tris(ligand) Co(III) compound blue single crystals of a binuclear Co(II) complex, Co$_2$L$_2$Cl$_4$, were formed.

Thermal analysis

The thermal decomposition of the compounds was studied by TG and DSC in flowing air and argon atmospheres with a heating rate of 10 K min^{-1}. In the case of Cu$_2$L$_2$Cl$_2$ a coupled TG-MS measurement was carried out in a helium atmosphere.

The decomposition pattern is similar in different atmospheres. On the contrary of our earlier experiences, in the case of the complexes with **L**, the decomposition in air is slower than in an inert atmosphere. In addition, traces of decomposition products in platinum crucible influence the decomposition in air at higher temperatures [11].

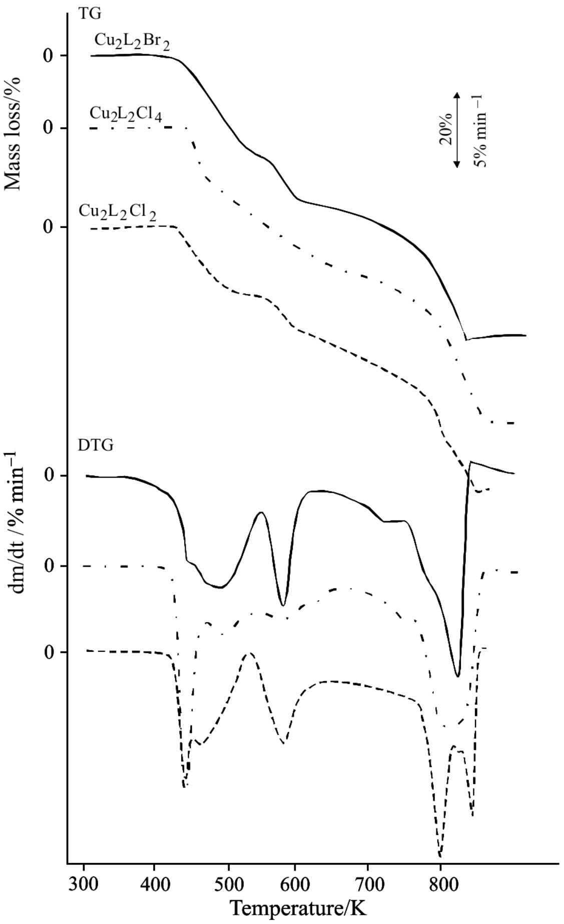


Fig. 1 TG-DTG curves of Cu$_2$L$_2$Cl$_4$, Cu$_2$L$_2$Br$_2$ and Cu$_2$L$_2$Cl$_2$ in argon

The TG-DTG curves of Cu$_2$L$_2$Cl$_4$, Cu$_2$L$_2$Br$_2$ and Cu$_2$L$_2$Cl$_2$ in argon are presented in Fig. 1 which clearly shows that the thermal stability of the copper complexes is about the same. All three complexes begin to decompose in a temperature range of 410–430 K. The decomposition of Cu$_2$L$_2$Cl$_4$ and Cu$_2$L$_2$Br$_2$ complexes is continuous in the whole range. The decomposition of Cu$_2$L$_2$Cl$_4$ starts at 425 K and consists of several superposing processes. The mass loss to the first minimum of the DTG-curve probably belongs to evaporation of 2HCl molecules (12%, calcd: 12.59%). This proposition is supported by the fact that the yellow-green single crystals of Cu$_2$L$_2$Cl$_4$ transform to orange modification spontaneously during long standing at room temperature. In argon at 850 K the end product is Cu$_2$S (26.5%, calcd: 27.47%) while in air the decomposition is not completed up to 1000 K. The decomposition of Cu$_2$L$_2$Br$_2$ starts at 415 K and the steps are somewhat better separated compared to Cu$_2$L$_2$Cl$_4$. The first superposed mass losses may correspond to loss of 2HBr molecules (25%, calcd: 27.09%). The decomposition is completed at 840 K in argon and at 855 K in air (Cu$_2$S%, 27.8 Ar, 25.0 air, calcd: 26.64).

The decomposition of Cu$_2$L$_2$Cl$_2$ takes a different course. It begins at 420 K. At 530 K a low stability intermediate is formed which was isolated and its FTIR spectrum was recorded. The characteristic

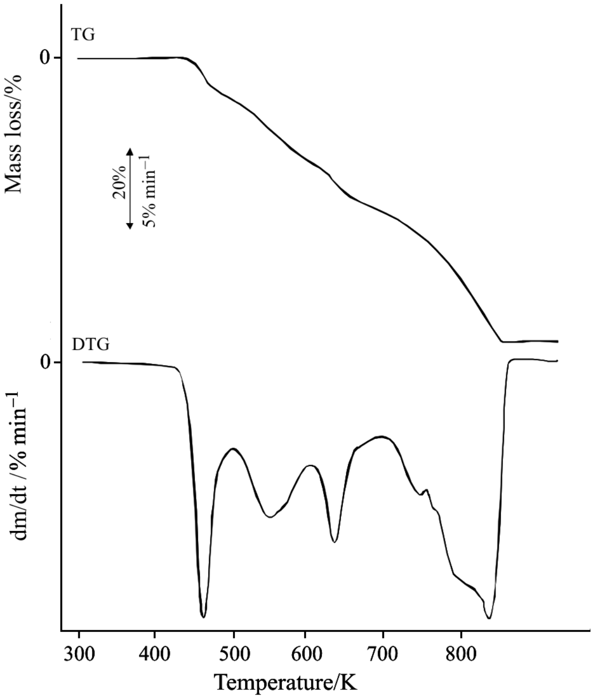


Fig. 2 TG-DTG curves of Co$_2$L$_2$Cl$_4$ in argon

vibrations of thioamide-group and the pyrazole ring are still present in the spectrum of the intermediate (3259b, 1627w, 1552w, 1526m, 1406s, 1042m, 980sh, 608m cm^{-1}) together with a very strong band at 2173 cm^{-1} referring to the formation of an SCN-group. To examine the course of decomposition we carried out a coupled TG-MS measurement in a He atmosphere in aluminum crucible. However, the decomposition in helium is even faster than in argon. The successive decomposition steps are almost inseparable and in a temperature range of 420–480 K CuSCN (47.5%, calcd: 47.84%) is formed. During the decomposition we were able to detect only fragments with significant intensity belonging to *m*/*z* of 64, 28 or C_5H_4 and N_2, i.e. they do not help in explaining the decomposition mechanism. In argon and air up to 530 K the mass loss is 17.5% which may correspond to loss of a 3,5-dimethylpyrazole (calcd: 18.91%) which is consistent with appearing of the SCN-band in the IR spectrum of the intermediate.

It is usual that the thermal decomposition patterns of isomorphous compounds are very similar. However, the mass loss for the first decomposition step of the corresponding bromine compound with departure of a dimethylpyrazole molecule would amount only 16.08% which is significantly less than the observed one (25%) referring to compounds with different structure.

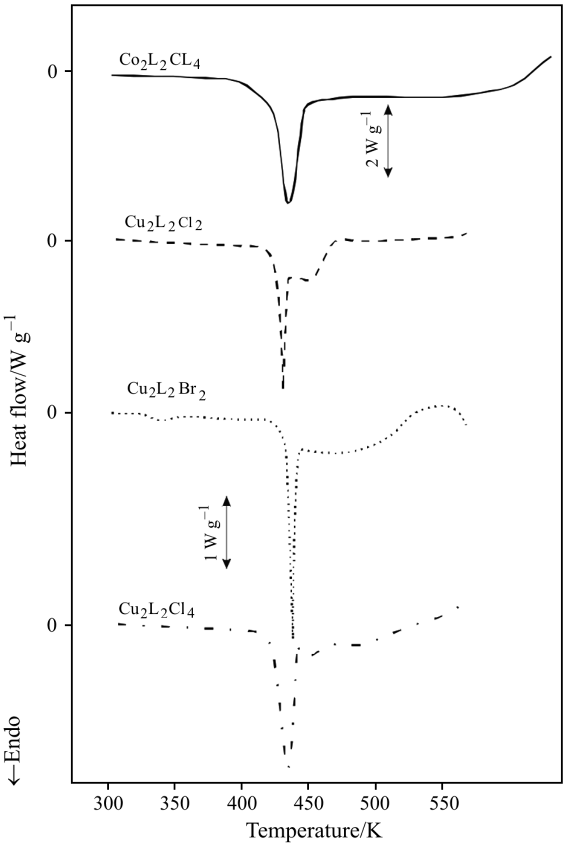


Fig. 3 DSC curves

The thermal stablilty of $Co_2L_2Cl_4$ (Fig. 2) is somewhat higher (445 K) than the stability of $Cu_2L_2Cl_4$ and $Cu_2L_2Br_2$ with a probably similar course of decomposition (–2HCl: 10%, calcd: 12.79%). At 850 K in argon (air 900 K) CoS is formed (Ar 30.8%, air, 34.1%, calcd: 31.89%) which up to 1040 K in argon decomposes to Co (21.6%, calcd: 20.67%) while in air the end product is an oxide (27.8%, calcd. (CoO): 26.29%).

The first sharp endothermic DSC peak (Fig. 3) may refer to a decomposition accompanied with melting of all four compounds. However, the visual observation shows that there is no melting in the case of $Cu_2L_2Cl_2$. The decomposition of $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$, $Co_2L_2Cl_4$ complexes above 500 K is accompanied with an exothermic effect, while the decomposition of $Cu_2L_2Cl_2$ is endothermic up to 600 K.

Conclusions

The 3,5-dimethyl-1-carboxamidpyrazole ligand, **L**, in the reaction with $CuCl_2$, $CuBr_2$ and $CoCl_2$ takes part in a bidentate (N, S) coordination which is found by single crystal X-ray analysis in $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$, $Co_2L_2Cl_4$ complexes. The same type of coordination mode is proposed for $Cu_2L_2Cl_2$ on the basis of FTIR data. However, the X-ray patterns and the FTIR-data of $Cu_2L_2Cl_2$ and $Cu_2L_2Br_2$ are not relevant to decide whether the corresponding chloro and bromo complexes are isostructural. For this purpose a more detailed X-ray analysis is proclaimed by pronounced preferred orientation effects observed in pattern and cannot be undertaken until powder diffraction data in capillary mode are collected.

The different thermal decomposition pattern of $Cu_2L_2Cl_2$ may refer to bridging chloro atoms instead of sulfurs. Namely, the structure of all three $Cu_2L_2Cl_4$, $Cu_2L_2Br_2$ and $Co_2L_2Cl_4$ complexes includes two terminal halide atoms and as a consequence during their thermal decomposition the first leaving molecules are most probable hydrohalides. On the contrary, $Cu_2L_2Cl_2$ decomposes to an intermediate with SCN-group. This phenomenon may be explained only with dimethylpyrazole departing fragments instead of hydrochloride. This would be consistent with the bridging chlorine atoms in $Cu_2L_2Cl_2$.

The reduction of Cu(II) to Cu(I) during complex formation is spontaneous in the bromine compound due probable to higher reducing ability of Br^- ion relative to Cl^-. The reduction of Cu(II) in the presence of chloride ion is promoted by the excess of **L** and higher temperature. The thermodynamically more stable compounds are those of Cu(I) with a more favorable soft–soft

Cu(I)–S (Br) interaction (in the case of bromine compound). These complexes are also sterically stabilized.

Acknowledgements

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