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TRANSITION METAL COMPLEXES WITH PYRAZOLE-BASED LIGANDS
7. Zn(II), Co(II), Mn(II) and Cu(II) complexes with 3-amino-5-methylpyrazole

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Abstract

Complexes represented by the general formula $[MCl_2L_2]$ (M(II)=Zn, Mn, Co) and complexes of $[Cu_3Cl_6L_4]$ and $CuSO_4L_2\cdot 4H_2O$, $CoSO_4L_2\cdot 3H_2O$, $[ZnSO_4L_3]$ where L stands for 3-amino-5-methylpyrazole were prepared. The complexes were characterized by elemental analysis, FT-IR spectroscopy, thermal (TG, DTG, DSC and EGA) methods and molar conductivity measurements. Except for the Zn-complexes, the magnetic susceptibilities were also determined.

Thermal decomposition of the sulphato complexes of copper(II) and cobalt(II) and the chloro complexes of cobalt(II) and manganese(II) resulted in well-defined intermediates. On the basis of the IR spectra and elemental analysis data of the intermediates a decomposition scheme is proposed.

Keywords: 3-amino-5-methylpyrazole, FT-IR spectroscopy, thermal decomposition, transition metal complexes

Introduction

In our previous paper [1] we investigated cadmium(II)-complexes with 3-amino-5-methylpyrazole and various anions (OAc$^-$, NCS$^-$, NCO$^-$, Cl$^-$ and SO_4^{2-}). Because of the involvement of a different anion, these compounds underwent to different thermal decomposition schemes. This paper deals with the synthesis, characterization and thermal decomposition of chloro and sulphato complexes of manganese, cobalt, copper and zinc with the same ligand.

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Experimental

IR spectra of the compounds were recorded in the range of 4000–450 cm^{-1} on a Perkin-Elmer System 2000 FT-IR spectrometer at room temperature using the KBr pellet technique. The spectra were obtained with a resolution of 4 cm^{-1} and with the co-addition of 16 scans.

Thermal analysis was performed using a DuPont 1090 TA system. The sample masses were about 5 mg. At the thermogravimetric measurements the samples were heated in a platinum crucible. The thermogravimetric decomposition curves of the chloro complex of cobalt(II) were recorded in both argon and air atmospheres at a heating rate of 10 K min^{-1}. Up to 600 K the decomposition curves were identical. As in argon the decomposition was not complete up to 1300 K, all other measurements were carried out in an air atmosphere heating the samples at a heating rate of 10 K min^{-1} to 950 K. DSC curves were obtained up to 600 K using an open aluminium pan as sample holder and an empty aluminium pan as reference.

EGA measurements were accomplished on a DuPont 916 TEA (Thermal Evolution Analyser) instrument in a flowing nitrogen atmosphere and a heating rate of 8 K min^{-1} to 600 K.

Molar conductivity of freshly prepared 10^{-3} mol dm^{-3} solutions of the compounds in an appropriate solvent was measured at room temperature using a digital conductivity meter (Jenway 4010).

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

Results and discussion

The compounds were prepared by reaction of hot solutions of the respective M(II)-salts in a suitable solvent (Table 1) with a hot solution of 3-amino-5-methylpyrazole (*L*) in ethanol. The salt-to-ligand mole ratio was 1:2. In spite of this

Table 1 Some physico-chemical properties of the complexes

Compound	Solvent for preparation	Colour	μ_{eff} in B.M.	λ_M^* in S/ $cm^2 mol^{-1}$
$[ZnCl_2L_2]$	EtOH	white	–	28.5^a
$[MnCl_2L_2]$	EtOH	white	5.79	94.8^a
$[Co(\mu\text{-}Cl)_2L_2]_n$	Me_2CO	pink	4.79	15.3^b
$[Cu_3Cl_6L_4]$	EtOH	olive-green	1.83	insoluble
$[ZnSO_4L_3]$	MeOH	white	–	insoluble
$CoSO_4L_2{\cdot}3H_2O$	H_2O	pink	4.84	191.7^c
$CuSO_4L_2{\cdot}4H_2O$	H_2O-EtOH	green	1.88	11.7^b

^{a} MeOH; ^{b} DMF; ^{c} H_2O

mole ratio, with zinc sulphate a tris(ligand), while in the case of the copper(II) chloride a trinuclear tetrakis(ligand) complex was obtained.

Selected physico-chemical properties of the compounds are given in Table 1. The chloro copper(II) and sulphato zinc(II) complexes are insoluble in DMF, MeOH, EtOH, Et_2O and H_2O. The other compounds are soluble in DMF, less soluble in MeOH and EtOH, while insoluble in H_2O and Et_2O except the chloro cobalt(II) complex which is soluble only in H_2O.

The composition and structure of the compounds were determined on the basis of elemental analysis and IR spectra. Magnetic susceptibilities were measured for all the complexes, except for the zinc compounds.

The X-ray analysis of $[ZnCl_2L_2]$ showed a tetrahedral arrangement around the central atom [2] which is characteristic for the majority of the zinc complexes [3]. It is established by coordination of two ligand molecules through the N(2)-nitrogen atoms of the pyrazole rings and two chloride ions. The low molar conductivity of the compound refers to the coordination of the chlorides even in solution.

The very intense band at 1115 cm^{-1} and the low intensity band at 1035 cm^{-1} in the IR spectrum of the $[ZnSO_4L_3]$ suggest a monodentate coordination of the sulphato group [4], so the tetrahedral geometry in this complex is established, beside of the coordination of the mentioned group, by coordination of three ligand molecules.

For the $[MnCl_2L_2]$ complex also a tetrahedral geometry may be supposed. The high molar conductivity of the methanolic solution of this compound corresponds to the value for an electrolyte of 1:1 type. This means that in the solution an

$$[MnCl_2L_2] + MeOH \rightleftharpoons [MnClL_2(MeOH)]^{+} + Cl^{-}$$

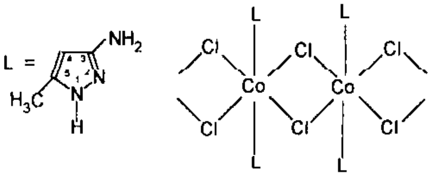
equilibrium is established. In addition, a formation of a hexacoordinated specimen may be also possible in the solution. The value of the magnetic susceptibility, μ_{eff}, for this compound (Table 1) is in agreement with the spin-only value for the system with $S=5/2$.

The μ_{eff} value and the colour of the sulphato and chloro cobalt(II) complexes (Table 1) suggest their octahedral geometry. In both of them an N(2)-coordination of the ligand molecules is supposed. In the sulphato complex beside the coordination of the SO_4-group and two ligand molecules three molecules of water are involved in the coordination. The λ_M value of the aqueous solution of the compound is close to the value for 1:2 electrolytes suggesting the presence of an uncoordinated sulphate ion in the solution.

The low molar conductivity of the polynuclear $[Co(\mu\text{-}Cl)_2L_2]$ complex refers to coordinated chloride ions even in solution. The octahedral geometry is most probably established through Cl–bridges (Scheme 1), as is usual in complexes with the mentioned stoichiometry [3].

The μ_{eff} value (Table 1) of the copper(II) complexes is characteristic for a d^9-system. The low solubility of the chloro complex may suggest its polymeric structure.

In the IR spectrum of the $CuSO_4L_2{\cdot}4H_2O$ compound the asymmetric $\nu(SO_4)$ band in the 1200–950 cm^{-1} range refers to a coordinated SO_4-group [5]. Its low λ_M value



Scheme 1

suggests the coordination of this group in solution also in contrast to the sulphato Co(II) complex whose SO_4-group in solution is not coordinated.

Similarly to the cadmium complexes [1], it was found that the course of thermal decomposition of the compounds depend on the anion. Additionally, the decomposition temperatures vary slightly with the cation and the stability of the intermediates is also cation dependent. The thermal decomposition data for the complexes are given in Table 2. The DSC curves are presented in Figs 1 and 2, the thermogravimetric decomposition curves in Figs 3 and 5, while the EGA curves of the sulphato copper(II) and chloro manganese(II) complexes in Fig. 4.

Table 2 Thermal decomposition data of the samples

Compound	Temp. range/ K	Mass loss/%		Temp. range/ K	Mass loss/%	
		found	calc.		found	calc.
$[ZnCl_2L_2]$	510–630	25.5	25.75[1]	670–770	11.0	9.42[2]
$[MnCl_2L_2]$	500–570	26.0	26.60[1]	570–630	12.0	11.38[2]
$[Co(\mu\text{-}Cl)_2L_2]_n$	500–620	28.5	26.27[1]	620–720	11.0	11.25[2]
$[Cu_3Cl_6L_4]$	440–470	3.5	3.92[3]	–	–	–
$[ZnSO_4L_3]$	470–540	24.0	28.31[4]	540–560	7.0	6.85[3]
$CoSO_4L_2{\cdot}3H_2O$	320–470	11.8	13.40[5]	470–490	6.5	7.70[3]
$CuSO_4L_2{\cdot}4H_2O$	300–360	16.3	16.92[5]	370–510	6.5	7.29[3]

[1] according to Scheme 3; [2] HCl evaporation; [3] according to Scheme 2; [4] ligand evaporation; [5] dehydration

The sharp endotherms in the DSC curves of the chloro complexes (Fig. 1) around 470 K are due to melting of the samples. The melting temperatures depend on the nature of the cation and increase in the order of copper(II) → cobalt(II) → zinc(II) → manganese(II) compound.

In the sulphato complexes no melting was observed. The first endothermic peak on the DSC curves of the $CoSO_4L_2{\cdot}3H_2O$ and $CuSO_4L_2{\cdot}4H_2O$ below 400 K correspond to the dehydration of the samples. The dehydration of the sulphato copper(II) complex starts at lower temperature and the anhydride is stable in a temperature range of about 100 K (Figs 2 and 3). The mass loss for the dehydration (TG curve in Fig. 3) is in agreement with the theoretical value. The dehydration of the sulphato cobalt(II) complex begins at higher temperature and the dehydrated sample decom-

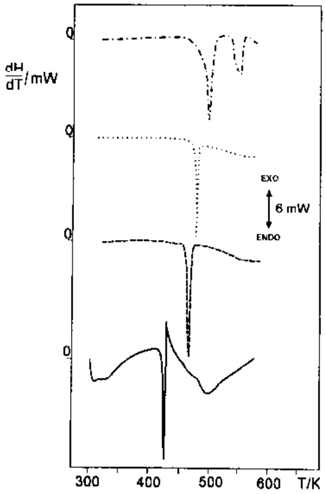


Fig. 1 DSC curves of the chloro complexes of copper(II) (—), cobalt(II) (- - -), zinc (···) and manganese(II) (-·-·-)

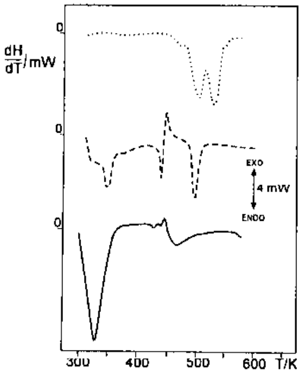


Fig. 2 DSC curves of the sulphato complexes of copper(II) (—), cobalt(II) (- - -) and zinc (···)

poses immediately (Figs 2 and 3). The water loss is somewhat less than expected. The dehydration in both of the complexes is followed by several decomposition processes in the range of 440–570 K. The product of the decomposition is an intermediate.

The thermal stability of the [$ZnSO_4L_3$] is higher than in the case of the sulphato Cu(II) and Co(II) complexes and most probably begins with the departure of a ligand molecule. Above 550 K the dropping of the DTG curve to zero refer to an intermediate formation, but its thermal stability is low and the decomposition proceeds almost immediately.

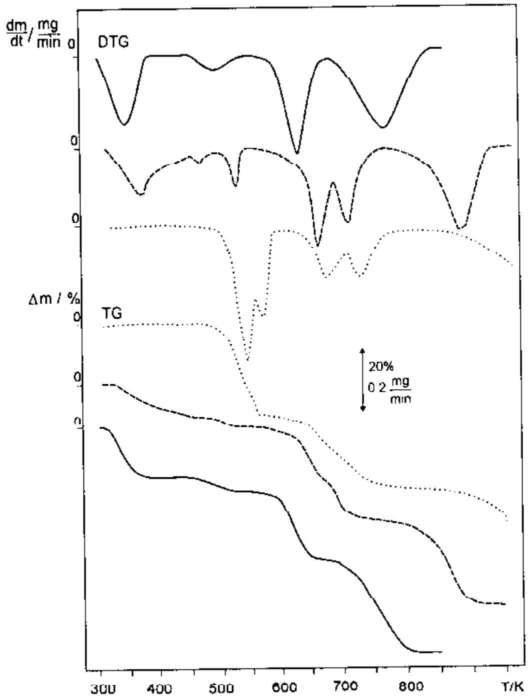
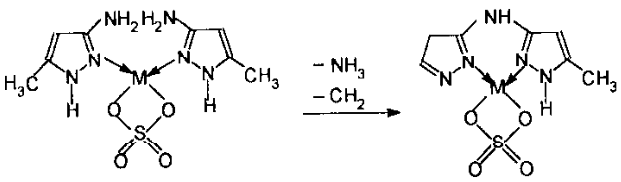


Fig. 3 TG and DTG curves of the sulphato complexes of copper(II) (—), cobalt(II) (- - -) and zinc (···)

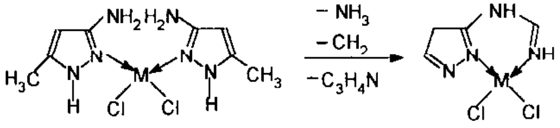
According to TG–DTG, DSC and EGA curves (Figs 2–4) the decomposition scheme of the sulphato complexes is very similar. The intermediates of the sulphato compounds were isolated by freezing out techniques, and the IR spectra of the intermediates were recorded. A common feature of all the spectra is disappearance of the characteristic ν(NH_2) vibrations. The broad band around 3300 cm^{-1} can be ascribed to ν(NH) vibrations. In the IR spectra of the intermediates a new band appears around 1440 cm^{-1} which can be assigned to the δ(CH_2) vibration. This fact together with the missing ν(NH_2) bands suggests a decomposition scheme depicted in Scheme 2 for all complexes with sulphate anion.



Scheme 2

The proposed scheme is supported by the amounts of mass losses as well as by the elemental analysis data of the sulphato copper(II) intermediate [calculated for $C_7H_8N_5CuCl_2$ (M_r=296.63): C, 25.19; H, 4.13; N, 20.99 %. Found: C, 26.42; H, 2.85; N, 22.01 %).

Above the dehydration temperature the EGA curve of the sulphato copper(II) compound (Fig. 4) indicates the departure of an organic decomposition fragment. The mass loss between the minima in the DTG curve of the sulphato cobalt(II) compound, where the decomposition steps are better separated, corresponds to the departure of a CH_2-fragment in accordance with the proposed scheme.



Scheme 3

Above 550 K all intermediates decomposes further with a departure of organic fragments up to 620 K, where the decomposition proceeds with inorganic fragments (Fig. 4). The end products contain oxides and sulphates (determined by a qualitative reaction) in the case of the sulphato copper(II) and cobalt(II) complexes while the end product of the decomposition of the sulphato zinc(II) compound is oxide.

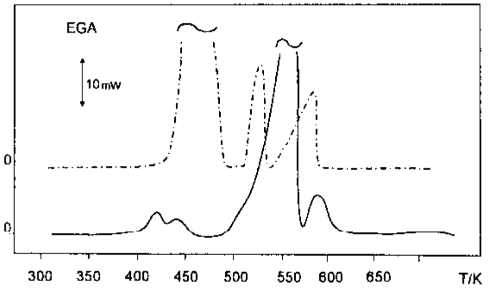


Fig. 4 EGA curves of the sulphato copper(II) (—) and chloro manganese(II) (-·-·-) compounds

The decomposition of the chloro complexes takes a different course. During the decomposition of the chloro M(II) (M=Co, Mn) complexes the formation of a relatively unstable intermediate was observed. According to TG–DTG curves (Fig. 5), the course of the decomposition of the other two chloro complexes are very similar to those of the chloro Co(II) and Mn(II) compounds. However, the instability of the formed compounds hindered their preparation. The IR-spectrum of the chloro cobalt(II) intermediate (500–620 K) is very similar to the spectra of the sulphato compounds. The missing ν(NH_2) band and the δ(CH_2) band around 1400 cm^{-1} may suggest the decomposition scheme presented in Scheme 2 also for the chloro Co(II) complex. However, the mass loss is not in complete agreement with this proposition. According to the TG data in the case of the chloro complexes Scheme 3 may de-

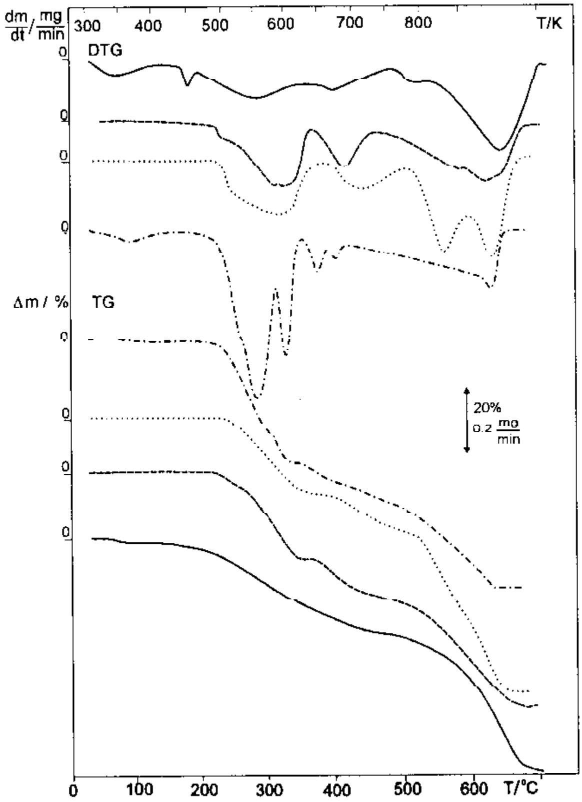


Fig. 5 TG and DTG curves of the chloro complexes of copper(II) (—), cobalt(II) (- - -), zinc (···) and manganese(II) (-·-·-)

scribe the first step of the decomposition. In this scheme the elimination of an ammonia molecule and a CH_2 group is accompanied by splitting of one of the pyrazole rings.

The TG curve of the chloro copper(II) complex indicates the presence of moisture in the original sample. The mass loss around 440 K (ca 2%) may correspond to an NH_3 and $-CH_2$ elimination. In this case, in spite of the different structure of the copper(II) compound, the first step of its thermal decomposition is similar to those of the other complexes.

The end products of the decomposition of the chloro compounds are oxides: cobalt(III), manganese(II) and copper(I) oxide (even in an air atmosphere), while in the case of $[ZnCl_2L_2]$ an additional mass loss was observed which can be attributed to a partial evaporation of $ZnCl_2$ above 900 K.

In the case of the chloro and sulphato copper(II) and sulphato cobalt(II) complexes (Figs 1 and 2) the NH–bridge formation is an exothermic process.

Conclusions

The chloro complexes of manganese(II) and zinc(II) may be characterized by a tetrahedral structure. In contrast, the cobalt(II) compound with the same anion have an octahedral geometry accomplished by bridge formation through the chloride atoms. The chloro copper(II) complex has most probably a polymeric structure. For the sulphato cobalt(II) and copper(II) compounds an octahedral geometry is characteristic which is achieved by additional coordination of molecules of water, while the sulphato zinc compound has a tetrahedral structure.

Thermal decomposition of Co(II) and Cu(II) sulphato and Co(II) and Mn(II) chloro complexes results in a well-defined intermediate around 550 K. The decomposition of the chloro complexes takes place at higher temperatures with a decomposition scheme slightly different from that of the sulphato complexes.

The decomposition of the compounds is complete around 900 K. In contrast to the intermediates, the composition of the end products is not well defined. In the case of the sulphato copper(II) and cobalt(II) complexes the end product is a mixture of sulphate and oxide. The decomposition of the $[ZnSO_4L_3]$ and M(II)-chloro (M=Co, Cu and Mn) complexes ends in oxides. In the chloro Zn(II) complex a partial evaporation of the zinc chloride was observed.

The course of the decomposition is determined by the anion as was observed also in imidazol complexes [6]. On the other hand, both the decomposition temperatures and the stability of the intermediates vary slightly with the cations.

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References

1 Mészáros-Szécsényi, E. Z. Ivegeš, V. M. Leovac, Lj. S. Vojinović, A. Kovács, G. Pokol, J. Madarász and Ž. K. Jaćimović, Thermochim. Acta, 316 (1998) 79.
2 Ž. K. Jaćimović, B. V. Prelesnik, G. A. Bogdanović, E. Z. Iveges and V. M. Leovac, Z. Kristallogr., 213 (1998) 35.
3 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, J. Wiley, New York 1989.
4 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York 1986.
5 M. S. Barvinok and L. G. Lukina, Zhur. Neorg. Khim., 28 (1983) 1993.
6 M. Rzepka and K. Zurowski, J. Thermal Anal., 48 (1997) 1357.