TRANSITION METAL COMPLEXES WITH PYRAZOLE-BASED LIGANDS
Part 8. Characterization and thermal decomposition of zinc(II) complexes with di- and trisubstituted pyrazoles

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Abstract

We report the synthesis and the characterization (elemental analysis, FT-IR spectroscopy, thermal methods and molar conductivity measurements) of the mixed complexes of zinc with acetate and 3-amino-5-methylpyrazole, HL^1, $[Zn(OAc)_2(HL^1)_2]$, or 3-amino-5-phenylpyrazole, HL^2, $[Zn(OAc)_2(HL^2)_2]$, or 4-acetyl-3-amino-5-methylpyrazole, HL^3, $[Zn(OAc)(L^3)(HL^3)]_2$, with isothiocyanate and HL^2, $[Zn(SCN)_2(HL^2)_2]$, or HL^3, $[Zn(SCN)_2(HL^3)_2]$, and with nitrate, isothiocyanate and 3,5-dimethyl-1-carboxamidinepyrazole, HL^4, $[Zn(NO_3)(NCS)(HL^4)_2]$.

The thermal decomposition of the complexes is generally continuous resulting zinc oxide as end product, except $[Zn(OAc)(L^3)(HL^3)]_2$, in which case a well-defined intermediate was observed between 570–620 K. On the basis of the IR spectra and elemental analysis data of the intermediate a decomposition scheme is proposed.

Keywords: 4-acetyl-3-amino-5-methylpyrazole, 3-amino-5-methylpyrazole, 3-amino-5-phenyl-pyrazole, FT-IR spectroscopy, thermal decomposition, zinc(II) complexes

Introduction

The biological activity of pyrazole and its derivatives is well known [1]. The utilisation of these compounds extends from the role as inhibitor of the alcohol dehydrogenase [2, 3] to their potential antiallergic action [4]. Some pyrazole derivatives may even inhibit the induction of mutations of some carcinogens [5].

On the other hand, metal ions, especially transition metal ions, play an important role in biological systems. For example, several enzymes are metal complexes where the coordination environment of the catalytically active metal ion may alter the activity of a specific enzyme. Hence, structural characteristics of transition metal complexes with bioactive ligands may be a valuable source of information. This work is a part of our studies on transition metal complexes with pyrazole-based ligands. In our previous paper [6] we reported on cadmium(II)-complexes with 3-amino-5-methylpyrazole and various anions, while in [7] we described the sulphato and chloro complexes of various cations (manganese, cobalt, copper and zinc) with the same ligand. In this paper we report the synthesis, selected physico-chemical properties and the thermal decomposition of acetato- and isothiocyanato complexes of zinc with different pyrazole-based ligands. Special attention was paid on the dependence of the geometry and thermal properties of the complexes on the nature of the pyrazole ring substituents and the coordinated anion.

Experimental

All pyrazole derivatives used were commercial products of the Aldrich Company except for 4-acetyl-3-amino-5-methylpyrazole, HL^3. The preparation of this ligand has been described elsewhere [8]. The compound 3,5-dimethyl-1-carboxamidinepyrazole, HL^4, was employed in the form of its nitrate salt.

The elemental analysis of the compounds was performed by standard micromethods in the Laboratory of Microanalysis at the Chemical Faculty of Belgrade.

The IR spectra of the compounds were recorded in the range of 4000–150 cm^{-1} on a Perkin Elmer System 2000 FT-IR spectrometer at room temperature using KBr pellets in the mid-IR range and polyethylene pellets in the far-IR range. The spectra were obtained with a resolution of 4 cm^{-1} and with a co-addition of 16 scans.

Thermal analysis was carried out using a DuPont 1090 TA system with samples of ca. 5 mg. At the thermogravimetric measurements the samples were heated in a platinum crucible. The thermogravimetric decomposition curves of the samples were recorded in air and for particular compounds also in nitrogen atmospheres at a heating rate of 10 K min^{-1} up to 1000 K. Some of the measurements were repeated at a heating rate of 2 and 5 K min^{-1}. The DSC curves were registered up to 600 K using an open aluminium pan as sample holder and an empty aluminium pan as reference. The 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).

Results and discussion

The compounds were prepared by a reaction of hot solutions of zinc acetate and the respective ligand in a suitable solvent (Table 1). The salt-to-ligand mole ratio was 1:2. By adding solid NH$_4$SCN to the reaction mixture, the corresponding isothio-

cyanato compound was formed, while the reaction of zinc nitrate, ammonium isothio-cyanate and 3,5-dimethyl-1-carboxamidinepyrazole, HL^4, resulted in the $[Zn(NO_3)(NCS)(HL^4)_2]$ complex.

Table 1 Composition of the compounds and elemental analysis data

	Compound[*]	M_r	Solvent for preparation	Found (calculated)/%		
				C	H	N
1	$[Zn(OAc)_2(HL^1)_2]$	377.76	MeOH	37.60 (38.15)	6.00 (5.41)	22.10 (22.25)
2	$[Zn(OAc)_2(HL^2)_2]$	501.90	MeOH	52.43 (52.64)	4.70 (4.83)	16.83 (16.75)
3	$[Zn(NCS)_2(HL^2)_2]$	499.97	MeOH	47.80 (48.04)	3.81 (3.64)	21.75 (22.42)
4	$[Zn(OAc)L^3(HL^3)]_2$	803.56	MeOH-DMF	42.23 (41.85)	4.91 (5.03)	20.46 (20.92)
5	$[Zn(NCS)_2(HL^3)_2]\cdot EtOH$	505.99	MeOH-DMF	37.67 (37.98)	4.09 (4.79)	22.61 (22.15)
6	$[Zn(NO_3)(NCS)(HL^4)_2]$	461.87	EtOH	34.02 (33.80)	4.87 (4.37)	30.51 (30.33)

[*]HL^1=3-amino-5-methylpyrazole, HL^2=3-amino-5-phenylpyrazole, HL^3=4-acetyl-3-amino-5-methylpyrazole, HL^4=3,5-dimethyl-1-carboxamidinepyrazole

Selected physico-chemical properties of the compounds are given in Table 2. The complexes are stable in air except for the $[Zn(NCS)_2(HL^3)_2]\cdot EtOH$ solvate, which loses the solvent at room temperature. Except the elemental analysis of this compound all other measurements were carried out with the desolvated sample. All the compounds are white crystals, well soluble in DMF, less soluble in MeOH and EtOH. As is usual for zinc compounds, the complexes are diamagnetic. The molar conductivity of $[Zn(NCS)(NO_3)(HL^4)_2]$ corresponds to the value for an electrolyte of 1:1 type, probably because of the $NO_3^- \leftrightarrow DMF$ exchange. The conductivity of the other isothiocyanato complexes is somewhat lower as a consequence of the

$$[Zn(NCS)_2(HL)_2]+DMF \leftrightarrow [Zn(NCS)(DMF)(HL)_2]^++NCS^-$$
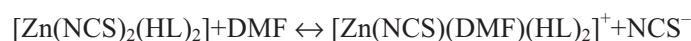
equilibrium, while the molar conductivity of the acetato complexes is significantly lower than that of the thiocyanato complexes, indicating the stronger coordination of the acetate anion.

The complex formation in these compounds is established through the pyridine nitrogen atom of the pyrazole ring which in the case of the $[Zn(OAc)_2(HL^2)_2]$ [9] and $[Zn(OAc)(L^3)(HL^3)]_2$ [10] complexes has been proven by X-ray analysis. In the $[Zn(OAc)(L^3)(HL^3)]_2$ compound an exobidentate coordination of the pyrazolato anion (L^3) is established through both of the nitrogen atoms. The tetrahedral arrangement around the zinc atom is achieved by dimer formation.

A single crystal of $[Zn(OAc)_2(HL^2)_2]$ can be obtained only in the presence of the solvent molecule and is stable only in the mother liquor. Hence, the structure of the

$[Zn(OAc)_2(HL^2)_2]\cdot 2MeOH$ solvate has been determined by Lindemann's capillary-mother liquor technique. The tetrahedral arrangement is accomplished by coordination of the pyridine nitrogens of the two pyrazole ligands and the two acetato groups.

Information on the coordination of the anions can be obtained from the IR spectra. In the case of the acetate ion unidentate, bidentate (chelate) or bridging coordination may be expected. The above coordination types can be distinguished using the $\Delta\nu=\nu_a(COO)-\nu_s(COO)$ values of the carboxyl group: $\Delta\nu>200$ cm^{-1} is characteristic on unidentate, $\Delta\nu<100$ cm^{-1} on bidentate coordination while $100<\Delta\nu<200$ cm^{-1} values refer to ionic or bridging complexes [11]. The $\Delta\nu$ values of 158 cm^{-1} for sample 1 and 165 cm^{-1} for 2 are in agreement with a bridging coordination of the acetate ion in these complexes where one of the oxygen atoms is coordinated to the metal while the other one is probably involved in hydrogen bonding with an NH hydrogen. In the case of 4, however, the $\Delta\nu=254$ cm^{-1} value refers to a unidentate coordination of the acetato group.

Table 2 Molar conductivity, IR-absorbance of the anion and the geometry of the compound

|	Compound	$\lambda_M/$ S cm^2 mol^{-1}	ν_{as} and ν_s (ν) of the anion/cm^{-1}	Geometry
1	$[Zn(OAc)_2(HL^1)_2]$	3.8	1560, 1402	tetrahedral
2	$[Zn(OAc)_2(HL^2)_2]$	3.0	1562, 1397	tetrahedral
3	$[Zn(NCS)_2(HL^2)_2]$	38.3	2090 (CN$^-$)	tetrahedral
4	$[Zn(OAc)L^3(HL^3)]_2$	19.8	1645, 1391	tetrahedral
5	$[Zn(NCS)_2(HL^3)_2]$	34.2	2090 (CN$^-$)	tetrahedral
6	$[Zn(NO_3)(NCS)(HL^4)_2]$	60.3	1500, 1250 (NO$_3^-$) 2100 (CN$^-$)	octahedral

The SCN group may be coordinated to the metal either through the nitrogen or the sulphur. The criteria for determining the bonding type must be taken with caution. In our case the position of the CN vibrational bands (the intensive IR-band below 2100 cm^{-1}, ~2090 cm^{-1}, 3; 2070 cm^{-1}, 5; 2100 cm^{-1}, 6), suggests that the coordinated atom is nitrogen [11]. In the IR-spectrum of the $[Zn(NO_3)(NCS)(HL^4)_2]$ the coordination of the nitrate group is indicated by the bands at 1500 and 1250 cm^{-1} [11] not present in the spectrum of the ligand. At the same time a very intensive band around 1380 cm^{-1} refers to the presence of an uncoordinated nitrate group [11]. However, as the IR-spectra were recorded using KBr pellet technique, this band may appear because of an $NO_3^- \leftrightarrow Br^-$ ion exchange between the compound and KBr, or it may belong to the traces of NH_4NO_3 formed during the synthesis of the compound. This means that both NO_3^- and Br^- are coordinated.

Additional characteristic feature of the $[Zn(NO_3)(NCS)(HL^4)_2]$ complex is that the HL^4 ligand may be coordinated not only through the pyridine nitrogen atom, but also through the imido-nitrogen of the carboxamidine group in agreement with a shift of the $\nu(C=NH)$ vibration at 1700 cm^{-1} in the free ligand towards lower frequencies

(1670 cm^{-1}). Such an N,N-coordination has been verified in the case of the [Cu(NO$_3$)$_2$(HL^4)$_2$] complex by X-ray analysis [12]. A similar N,N-coordination has been found also in 3,5-dimethyl-1-carboxamidepyrazole complexes with various cations [13, 14]. Based on the IR characteristics of the above complexes we can assume an octahedral geometry for the [Zn(NO$_3$)(NCS)(HL^4)$_2$] complex.

Thermal decomposition of the compounds

The thermal decomposition data are given in Table 3, the TG-DTG decomposition curves of the acetato compounds are presented in Fig. 1 and those of the isothiocyanato complexes in Fig. 2. As can be seen, the thermal stability of the acetato complexes is lower than the stability of the corresponding isothiocyanato complexes. The thermal stability of the dimeric acetato compound is close to the stability of the isothiocyanato complexes, while the stability of the nitrato-isothiocyanato complex is higher than that of the acetato compounds, but lower than the stability of the isothiocyanato complexes.
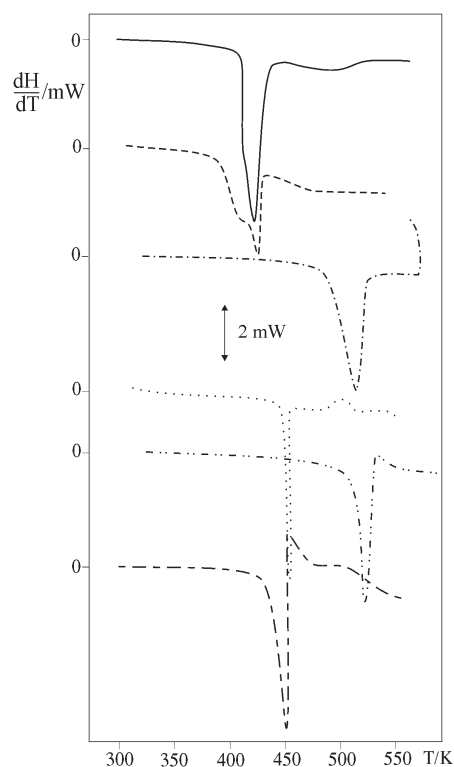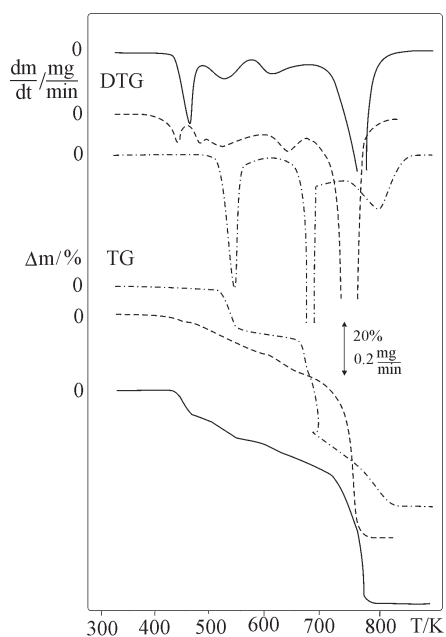

Fig. 1 DSC curves of the samples: [Zn(OAc)$_2$(HL^1)$_2$] (–), [Zn(OAc)$_2$(HL^2)$_2$] (---), [Zn(OAc)L^3(HL^3)]$_2$ (-·-·), [Zn(NCS)$_2$(HL^2)$_2$] (···), [Zn(NCS)$_2$(HL^3)$_2$] (– - –), [Zn(NO$_3$)(NCS)(HL^4)]$_2$ (-····-)

The DSC curves presented in Fig. 3 give information on the heat effects of the decomposition in the 300–600 K temperature range. The first sharp endothermic peak in the acetato compounds refers to the melting of the sample. The decomposition enthalpy of the following step depends on the anion: the decomposition of the iso-thiocyanato complexes exhibits a small exothermic effect, while the decomposition of the acetato complexes is an endothermic process.

Table 3 Thermal decomposition data of the compounds

	Complex	T_{range}/K	Mass change, found (calcd.)/%	T_{range}/K	Mass change, found (calcd.)/%
1	$[Zn(OAc)_2(HL^1)_2]$	420–580	19.0 (22.80)[*]	580–800	78.0 (78.46)
2	$[Zn(OAc)_2(HL^2)_2]$	420–600	15.0 (16.95)[*]	600–830	83.0 (83.78)
3	$[Zn(NCS)_2(HL^2)_2]$	500–740	31.0 (27.74)[3*]	740–940	84.0 (83.72)
4	$[Zn(OAc)L^3(HL^3)]_2$	570–620	17.0 (17.32)[2*]	640–920	81.0 (79.74)
5	$[Zn(NCS)_2(HL^3)_2]$	530–710	23.0 (27.98)[3*]	710–1000	82.0 (82.30)
6	$[Zn(NO_3)(NCS)(HL^4)_2]$	460–480	34.0 (34.57)[3*]	480–1000	83.0 (82.38)

[*]According to Scheme 3, [2*] According to Scheme 1, [3*] According to Scheme 2

Fig. 2 TG and DTG curves of the samples: $[Zn(NCS)_2(HL^2)_2]$ (—) , $[Zn(NCS)_2(HL^3)_2]$ (---), $[Zn(NO_3)(NCS)(HL^4)]_2$ (-··-)
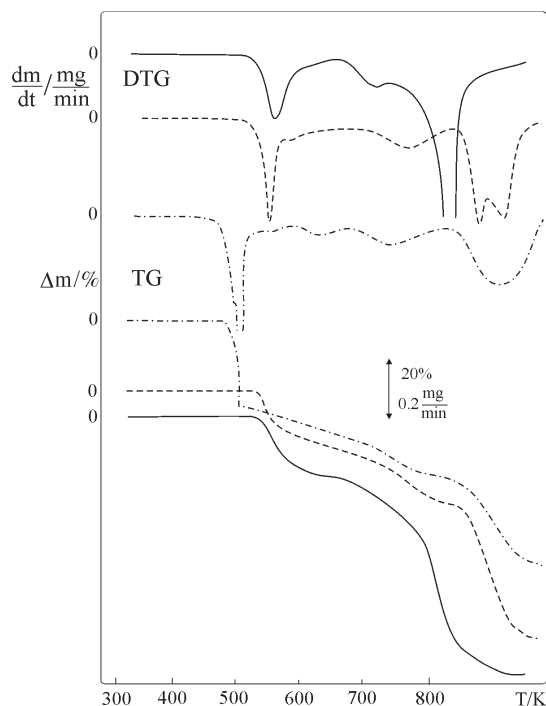
Fig. 3 TG and DTG curves of the samples: $[Zn(OAc)_2(HL^1)_2]$ (—),
$[Zn(OAc)_2(HL^2)_2]$ (---), $[Zn(OAc)L^3(HL^3)]_2$ (-·-·-)

The decomposition up to 600 K is independent on the nature of the gas carrier. In argon, the decomposition was not completed up to 1300 K. In air, the shape of the TG-DTG curves of the acetato complexes above 700 K refer to the burning of the sample, while the isothiocyanato complexes do no show such an effect. The final product of the decomposition in air is always ZnO.

During the decomposition of the compound with 4-acetyl-3-amino-5-methyl-pyrazole, $[Zn(OAc)(L^3)(HL^3)]_2$, an intermediate was formed which was stable in the range of 570–620 K. By freezing-out technique the intermediate was isolated and its composition was determined by elemental analysis. The IR spectrum of the intermediate was also recorded. The most characteristic changes with respect to the spectrum of $[Zn(OAc)(L^3)(HL^3)]_2$ are the disappearance of the NH_2 stretching vibrations and the appearance of a new NH stretching vibrational band at 3363 cm^{-1}. In the $1000–1700 \text{ cm}^{-1}$ range the C=O stretching band of the acetato group shifted to the lower wavenumbers by 11 cm^{-1} and the C–O stretching band (1406 cm^{-1}) lost intensity, while in the far-IR region the positions of the ZnO and ZnN stretching bands are significantly altered. These changes resemble our recent experience on 3-aminopyrazole complexes [6], where the two pyrazole moieties of a complex got connected by an –NH– bridge formed from the

two NH$_2$ groups parallel with an NH$_3$ elimination in the decomposition procedure. In the case of the [Zn(OAc)(L^3)(HL^3)]$_2$ compound the NH$_3$ elimination is probably followed with the loss of two acetato groups. The mass loss of 17.0% (calcd 16.20%) and the elemental analyses data (found (%) C-41.4; H-4.6; N-23.0, calcd (%): C-41.03; H-4.49; N-20.80) may support a decomposition mechanism presented by Scheme 1:
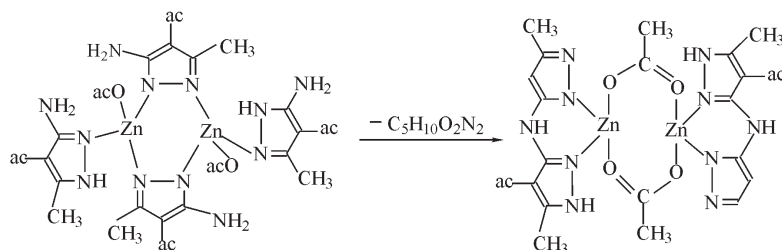
At the decomposition of the acetato complexes with 3-amino-5-methylpyrazole and 3-amino-5-phenylpyrazole also an NH$_3$ elimination takes place. However, in these complexes probably the splitting of the pyrazole ring occurs during the decomposition. As the decomposition of these compounds is continuous, it is difficult to propose the decomposition mechanism. We can assume an analogy with the decomposition of sulphato M(II) complexes with 3-amino-5-methylpyrazole [6] where the stable intermediates were observed and identified. Comparison of the TG-DTG curves of the [Zn(OAc)$_2$(HL^1)$_2$] and [Zn(OAc)$_2$(HL^2)$_2$] compounds with the corresponding ones from [6], as well as the mass loss during the decomposition suggest that the decomposition of these complexes takes place in a similar way as in [6] (Scheme 2):
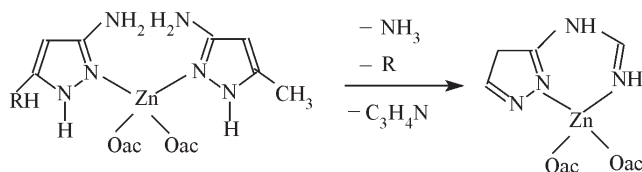
No intermediate formation was observed in the case of the decomposition of the isothiocyanato complexes either. The mass loss (Table 1) up to the second minimum of the DTG curve may correnspond to Scheme 3.
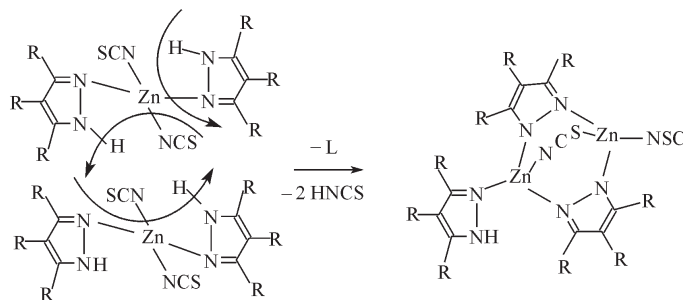
However, the decomposition of these samples is continuous, thus an intermediate could not be isolated.

Conclusions

A tetrahedral geometry is characteristic of all of the complexes, except the complex with 3,5-dimethyl-1-carboxamidinepyrazole, $[Zn(NO_3)(NCS)(HL^4)_2]$ which has an octahedral configuration. The geometry of these complexes is determined above all by the nature of the substituent on the pyrazole ring. As there is no possibility for a stabilization by ligand field stabilization energy (LFSE), the stereochemistry of the Zn-complexes depends on the cation size and on steric factors of the ligand. In these complexes, the ring substituents with additional donor atoms may serve for formation of complexes with a higher coordination number. So, 3,5-dimethyl-1-carboxamidine-pyrazole is coordinated to the zinc atom through the N,N-atoms leading to an octahedral structure in the $[Zn(NO_3)(NCS)(HL^4)_2]$ complex.

The thermal stability of the compounds is mostly anion dependent. However, the decomposition mechanism depends not only on the anion type but also on the pyrazole ring substituent. The thermal decomposition of the complexes with 3-amino substitution takes place by losing of NH_3-molecule ([6] or H_2O, [7]) which may be followed by a splitting of one of the pyrazole rings as is presented in Scheme 2. In the case of the acetato or isothiocyanato complexes there is a possibility of the intermediate stabilization through an additional bond formation *via* the anion (Scheme 3 and [7]). The stability of the acetato intermediates is most probably a consequence of the stability of the bridge. This proposition is also supported by the DSC curves of the compounds: while the second step of the decomposition of the isothiocyanato complexes exibits a small exothermic effect, the corresponding decomposition step of the acetato compounds is an endothermic process.

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