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TRANSITION METAL COMPLEXES WITH PYRAZOLE BASED LIGANDS
Part 15. Cobalt(III)-, nickel(II)- and copper(II)-complexes with 3,5-dimethyl-1-thiocarboxamidepyrazole

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Abstract

The complex formation of cobalt(II)-, nickel(II) and copper(II) sulphate hydrates with 3,5-dimethyl-1-thiocarboxamidepyrazole (HL) was studied. The influence of the anions on the course of the reaction was also examined, using nickel(II) salts with various anions. Beside the $NiSO_4·7H_2O$ the reaction has been carried out with $Ni(OAc)_2$, $Ni(CF_3COO)_2$ and $Ni(SCN)_2$. Compounds with the following composition were obtained: $Co(L)_3$, $Ni(L)_2$ and $[Cu(SCN)L]_2$. The structure of the ligand and the $Co(L)_3$ complex was determined by single crystal X-ray analysis, while that of the $Ni(L)_2$ was solved by analysis of powder diffraction X-ray data. The most probable structure of the copper(II) complex is proposed on the basis of the elemental analyses data, FT-IR spectrometry and magnetic measurement.

The thermal decomposition of the complexes was investigated by thermogravimetry, DSC and coupled TG-MS measurements. In the case of the nickel(II) compound, a relatively stable intermediate was detected in the 550–650 K temperature range. The composition of the intermediate, Ni(SCN)(NCS), was determined by FT-IR-spectrometry.

Keywords: cobalt(III)-, nickel(II) and copper(II) complexes, 3,5-dimethyl-1-thiocarboxamidepyrazole, FT-IR-spectrometry, thermal analysis

Introduction

Some natural products like distamycin A [1, 2] show a wide spectrum of antiviral and antitumor activities. Monopyrazole analogues of distamycin A display antiviral effect comparable to that of distamycin A [3].

The complexing ability of pyrazole derivatives is well known [4–6]. They are applied for the metal ion extraction [5], used in pharmaceutical industry as drug com-

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ponents, or components of herbicides and antifungal agents [7]. The azo-derivatives of the pyrazoles are important pigments for the synthetic leader and vinyl polymers [8], therefore their thermal stability is of great importance.

The active site of metall-proteins may be partly mimicked by simple models containing pyrazole ring which similarity in the electronic and steric sense to imidazoles, as parts of the histidine fragments of proteins [9], is significant but the former compounds are more readily synthesized. Recently, attention is paid to the design of various pyrazole ligands with special structural properties to fulfill the specific stereochemical requirements of a particular metal-binding site [10].

A monodentate coordination of the pyrazole derivatives is established through its pyridine nitrogen atom. The deprotonated pyrazole, the pyrazolide ion, can coordinate through both nitrogen atoms as a bidentate ligand. When the pyrazole ring has substituents with different donor atoms in position 1-, 3- or 5-, it can act as bridging or non-bridging polydentate ligand [11–15].

The aim of our systematic studies on transition metal pyrazole complexes is to investigate the influence of the pyrazole ring substituents on the course of the complex formation [16–18]. In this paper we have examined the reaction of cobalt(II)-, nickel(II) and copper(II) sulphate hydrates with 3,5-dimethyl-1-thiocarboxamidepyrazole (HL). The obtained compounds were $Co(L)_3$, $Ni(L)_2$ and $[Cu(SCN)L]_2$. Complexes of the former cations with analogues ligands, namely, with 3,5-dimethyl-1-N-methyl and 1-N-ethyl thiocarboxamidepyrazole are already known and structurally characterized [19, 20]. The structure of the 3,5-dimethyl-1-thiocarboxamidepyrazole ligand [21] as well as the structure of the $Co(L)_3$, obtained by the reaction of cobalt(II) acetate instead of cobalt(II) sulfate with the same ligand, has been determined by single crystal X-ray analysis [22]. Since the role of the anions in the reaction cannot be ruled out, we have used different nickel(II) salts to examine the influence of the anions on the complex formation. The complex formation has been carried out beside $NiSO_4$ also with $Ni(Oac)_2$, $Ni(SCN)_2$ and $Ni(CF_3COO)_2$. As a result, the same $Ni(L)_2$ complex was formed. The thermal stability of the compounds has been studied by thermogravimetry and DSC. For the better understanding of the thermal decomposition mechanism, the TG-equipment is often is combined with instruments for EGA [23]. In our case the TG was combined with MS.

Experimental

All chemicals used were reagent grade

The ligand was prepared by the reaction of thiosemicarbazide (5 g) and acetyl acetone (5 cm^3) in acidic aqueous solution (250 cm^3 H_2O+1 cm^3 cc. HCl) at room temperature. Reaction time: 6 h. The white precipitate was washed with water and dried at room temperature.

The complexes were synthesised by mixing of cold methanolic solutions of the appropriate metal(II) sulphate hydrate (1 mmol metal salt) and the ligand (2.5 mmol). The total volume of the solution after mixing was about 10 cm^3. As the solubility of

$CuSO_4 \cdot 5H_2O$ in methanol is very low, a saturated aqueous solution of the copper(II) sulphate was used instead of its solution in methanol. The reaction mixture was slightly heated about 10 min. In the case of the copper(II) compound an immediately precipitation was observed, while the other two compounds precipitated in 30 min. The obtained complexes were filtered after 4 h, washed with methanol and water and dried at room temperature.

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

The thermal analysis was carried out using a DuPont 2000 TA system with a thermobalance DuPont 951 TGA. At the thermogravimetric measurements the samples (ca. 5 mg) were heated in a platinum crucible with a heating rate of 10 K min^{-1} up to 1000 K in flowing air and argon atmospheres. With the same heating rate the DSC curves were registered up to 600 K using an open aluminium pan as sample holder and an empty aluminium pan as reference. For the TG-MS measurements a TA Instruments SDT 2960 was employed, coupled with Balzers Termostar GSD 300 T capillary MS. The measurements were conducted in flowing helium and air atmospheres.

The magnetic moment of the complexes was measured using a magnetic susceptibility balance MSB-MKI, Sherwood Scientific Ltd, Cambridge. The data were corrected for diamagnetic susceptibilities.

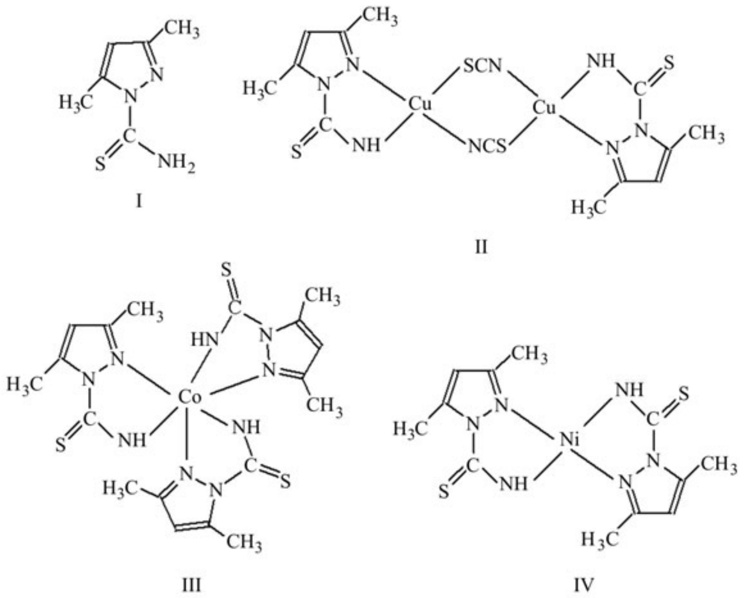
Results and discussion

The crystal and molecular structure of the ligand [21] and the $Co(L)_3$ complex were determined by single crystal X-ray analysis [22]. The FT-IR spectra of the cobalt(III) compounds obtained in the reaction of $Co(OAc)_2$ and $CoSO_4$ with HL were identical. The structure of the nickel(II) complex was solved on the basis of powder diffraction X-ray data earlier [22]. The structure of the ligand, **I**, the copper(II), **II**, cobalt(III), **III** and nickel(II), **IV**, complexes is presented in Scheme 1.

The elemental analysis data for the copper(II) compound ($CuC_7H_8N_4S_2$, M_r=276.85) are C: 28.04 (calcd. 30.37), H: 2.92 (calcd. 3.28), N: 18.56 (calcd. 20.24), Cu: 22.07 (calcd. 23.16)%.

All the compounds are colored and stable in air. The copper(II) complex is practically insoluble in the common solvents; compounds **III** and **IV** are soluble in DMS and DMF, less soluble in acetone, methanol and ethanol and insoluble in water. The low molar conductivity of the nickel(II) and cobalt(III) compound shows to their non-electrolytic character.

The lack of the magnetic moment of the cobalt compound points to the oxidation of the central atom during the complex formation in air, i.e. to the formation of a cobalt(III) complex. The nickel(II) compound is diamagnetic, referring to a tetra coordinated central atom which is in accordance with the determined *trans*-squere-planar structure of the complex. The magnetic moment of the copper(II) complex (μ_{eff}=1.53 μ_B) i.e. is somewhat less than the expected spin only value for the S=0.5 systems. This suggests a



Scheme 1

dimeric (polymeric) structure for this compound. The dimeric structure is supported also by the low solubility of the compound [23].

The most probable structure of the copper(II) compound is assumed on the basis of its IR spectrum [26], compared with the spectrum of the ligand [27].

The strong bands in the spectrum of the ligand in the 3400–3100 cm^{-1} range are characteristic for the primary amide ν(NH_2) vibrations (3398 cm^{-1} NH_2 stretch, 3241 and 3135 cm^{-1} asymmetric and symmetric stretch, respectively). In the spectrum of the complex the intensity of the ν(NH) vibration is lower and its position has changed to 3338 cm^{-1} referring to the deprotonation of the NH_2-group. The scissoring NH_2 bands in the spectrum of the ligand appear at 1600 and 1576 cm^{-1} together with pyrazole skeleton stretch vibrations. In the spectrum of the complex the strong band at 1600 cm^{-1} has almost completely vanished, supporting the proposition on the deprotonation of the amide-group. The β(NH) band is shifted to 1572 cm^{-1}. Bands at 808 and 802 cm^{-1} in the spectrum of the ligand and the copper(II) complex, respectively, can be assigned to the ν(CS) vibration. The intensity of the bands is about the same, suggesting that the sulphur atom does not take part in the coordination after the deprotonation.

The most significant difference in the FT-IR spectrum of the ligand and in the spectra of the cobalt(III) and nickel(II)-complexes compared with the spectrum of the copper(II) complex is the appearance of a strong band at 2116 cm^{-1} in the spectrum of the latter which can be assigned to the ν(SCN) vibration.

Structure **II** (Scheme 1) can be proposed as most probable for the copper(II) complex. The relatively large deviation between the calculated and experimentally determined results of the elemental analysis data may be a consequence of the impurity of the compound due to a very rapid precipitation process. The very low solubility of the complex made its purification by recrystallization impossible.

It is interesting to emphasize that in reaction of copper(II) chloride and bromide with the same ligand, the ligand is coordinated to copper(II) in its neutrale thio-keto form (unpublished data). The same coordination mode was found in copper(II) halide complexes with analogous 3,5-dimethyl-1-N-methyl and 1-N-ethyl thiocarboxamide-pyrazole ligand [19, 20]. This points to the important role of the anions in complex formation reactions.

The influence of the anions on the course of the reaction was investigated using different nickel(II) salts. Beside $NiSO_4$, the reaction was carried out under similar experimental conditions with salts containing anions of different Brønsted basicity: $Ni(CH_3COO)_2$, $Ni(CF_3COO)_2$ and $Ni(SCN)_2$. With $NiSO_4$ and $Ni(CH_3COO)_2$ a spontaneous reaction was observed. In the case of the other two salts the complex formation failed. However, addition of NaOH to the reaction mixture induced the precipitation with $Ni(CF_3COO)_2$ and $Ni(SCN)_2$ also. The infrared spectra of the formed compounds were in all the cases identical referring to formation of identical complexes.

The difference in complex formation in the case of $Ni(CH_3COO)_2$, $Ni(SCN)_2$ and $Ni(CF_3COO)_2$ may be explained by the decreasing Brønsted basicity of the anions. The basicity of the acetate ion is high enough for the deprotonation of the ligand taking into account the crystal field stabilization energy (CFSE), released during complex formation. In the case of the SCN^- and CF_3COO^- ions the deprotonation is promoted by adding of NaOH to the solution. The spontaneous reaction in the case of $NiSO_4$ cannot be explained on the basis of the Brønsted basicity of the sulfate ion. It is too low as compared to the basicity of the other three ions, while the CFSE remains the same. As a consequence, some other interactions should be considered, taking into account Pearson's soft-hard classification of the acids and bases [28–30]. According to the classification of the ions as soft or hard acids and bases, nickel(II) ion is a medium soft acid while CH_3COO^-, SCN^- and CF_3COO^- ions belong to medium soft bases. This assumes a stronger interaction between the ions; the interaction between the nickel(II) and the hard sulfate base is less explicit, promoting thus the reaction of Ni(II) with the ligand. The solvation energy of the ions in the same solvent are also different and probably cannot be ignored, either.

Thermal decomposition of the compounds

The thermogravimetrical and DSC curves of the ligand and the complexes were registred in air and argon atmospheres. The TG-DTG curves of the ligand in air and argon are presented in Fig. 1, while those of the complexes in air in Fig. 2. The DSC curves are depicted in Fig. 3.

As is usual, the thermal stability of the ligand is lower than that of the complexes (Figs 1 and 2). The endothermic decomposition of the ligand, accompanied by the melting (Fig. 3) begins at 360 K. In air, at 500 K the decomposition is completed when the measurement is carried out in an unused aluminum pan. When the decomposition is measured in a platinum crucible with traces of metal salts, the thermal sta-

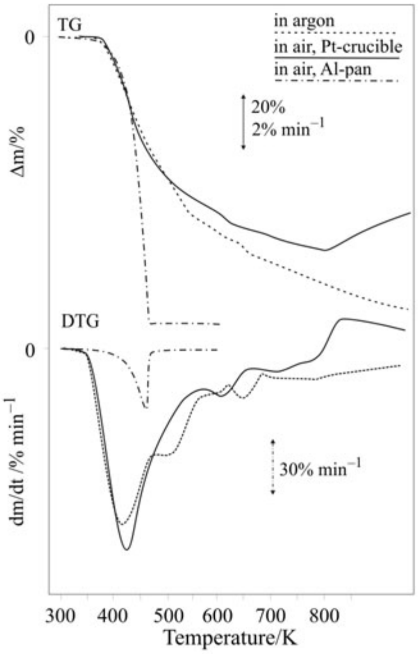


Fig. 1 TG and DTG curves of the ligand in air and argon atmosphere

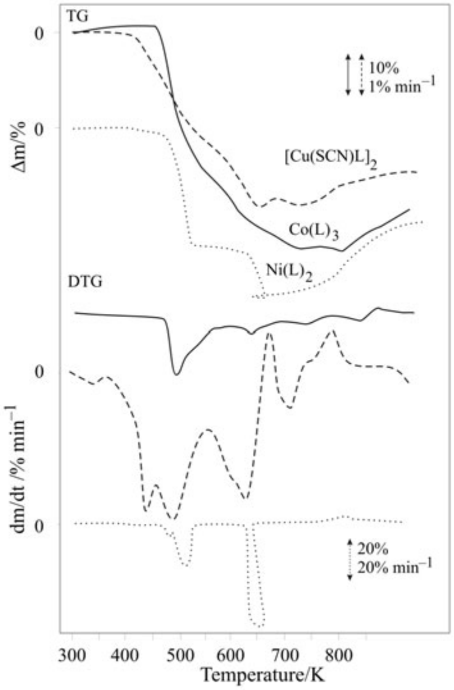


Fig. 2 TG and DTG curves of the complexes in air

bility of the ligand seems to be higher and above 800 K uncontrolled oxidation processes are taking place as was observed with some other thiocompounds [31]. The ligand decomposition in argon is also complete, but it is finished above 1000 K.

The thermal decomposition of the complexes starts at somewhat higher temperature. The highest thermal stability belongs to the cobalt(III) complex (Fig. 2, 440 K), while the thermal stability of the nickel(II) and copper(II) complexes is about the same (≈380 K). The decomposition of the complexes is endothermic. The sharp exothermic peak in the DSC curve of the nickel(II) complex is probably a consequence of a structural rearrangement.

The thermal decomposition of the nickel(II) compound was followed also by a coupled TG-MS measurement in a helium purge gas. The first decomposition step belongs to the fragmentation of the ligand, probably to demethylation of the pyrazole ring. By recombination of the methyl groups ethane molecules (m/z=30) or C_2H_7-fragments are forming. In Fig. 4 the m/z=31 amu is shown which probably belongs to the C_2H_7-fragment. Both of the peaks were also detected in the mass spectrum of the 3,5-dimethylpyrazole but with much less intensity [32]. At higher temperature the highest peak intensity in the mass spectrum is that with an m/z=28 which may be ascribed to a nitrogen evolution from the pyrazole ring. In air, the first peak belongs to m/z=44, i.e. the dominant process in the decomposition is an oxidation, resulting in CO_2 formation, but even in air peaks with m/z=30 and m/z=31 are detectable. Similar decomposition pattern was observed at the thermal decomposition of the $Cu(L^3)_2$ and $[CuBr(HL^1)(L^3)]_2$ complexes (HL^1=3,5-dimethylpyrazole, L^3=3,5-dimethyl-1-carboxamidepyrazolide ion) [33]. At 550 K an intermediate formation is detected which is stable in the 550–650 K temper-

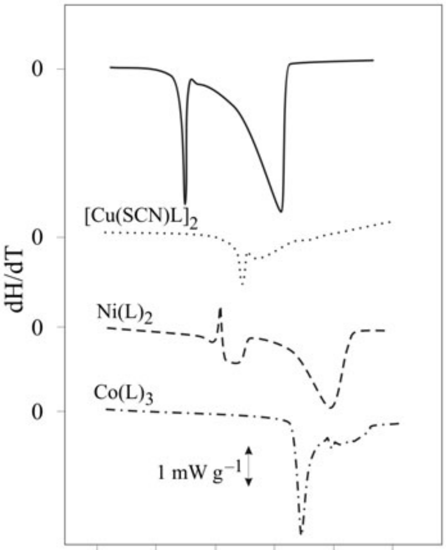


Fig. 3 DSC curves for the ligand and the complexes

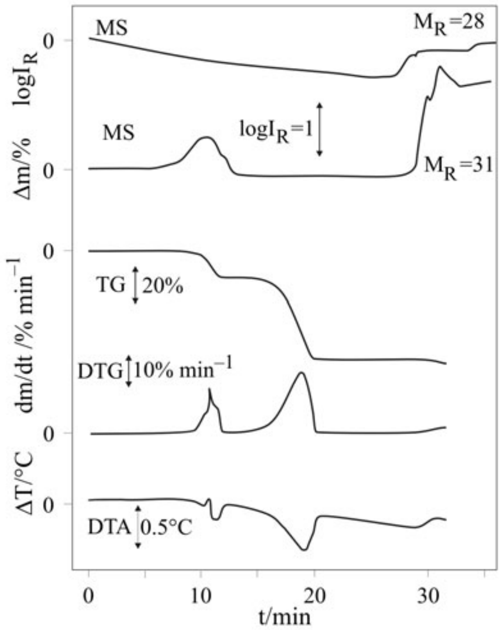


Fig. 4 TG–MS coupled curves for $Ni(L)_2$

ature range. The probable composition of the intermediate is $Ni(SCN)_2$ (Δm=46.9%, calcd.: 47.64 %). The FT-IR spectrum of the intermediate supports this proposition. Bands at 2167 and 2113 cm^{-1} can be assigned to ν(SCN) and ν(NCS) vibrations, thus the most probable composition of the intermediate is Ni(SCN)(NSC), i.e., the structure contains both thiocyanate and isothiocyanate ligands.

The decomposition of the other complexes is continuous. In the air above 650 K uncontrolled oxidation processes are taking place (probably because of the metal ion traces in the platinum crucible). In argon such phenomenon was not observed, but the decomposition of the complexes is not finished up to 1000 K.

Conclusions

The complex formation of hydrates of copper(II), nickel(II) and cobalt(II) sulfates with 3,5-dimethyl-1-thiocarboxamidepyrazole is accompanied by the deprotonation of the ligand. In the reaction in air a cobalt(III) complex, $Co(L)_3$ is obtained. The structure of the nickel(II) complex, $Ni(L)_2$, is *trans*-square planar [24], while in the case of copper(II) complex the reaction is accompanied also by the structural rearrangement of the ligand and a dimeric compound is formed with a probable composition of $[Cu(SCN)L]_2$.

The role of the anion in the reaction has been studied with various nickel(II) salts. The complex formation can be related to the basicity of the anions as well as to the interactions between the nickel(II) ion and the anions. The explanation of the interactions may be based on Pearson's theory. The solvation effect probably cannot be ignored, either.

The thermal stability of the compounds is low. The decomposition is endothermic in all the cases. The sharp exotherm peak in the case of the nickel(II) complex probably belongs to a structural rearrangement during the thermal treatment. The decomposition of the compounds is continuous except in the case of Ni(L)$_2$, where in the temperature range of 550–650 K an intermediate formation is observed. The composition of the intermediate on the basis of its FT-IR spectrum is Ni(SCN)(NCS). In argon the decomposition of the ligand is completed above 1000 K, while the decomposition of the complexes is not complete in this temperature range. In air above 650 K uncontrolled oxidation processes are taking place, probably catalysed by traces of metal salts in the platinum crucible.

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