

TRANSITION METAL COMPLEXES WITH PYRAZOLE BASED LIGANDS Part XXV. Deaquation of isostructural cobalt(II) and nickel(II) complexes with 3,5-dimethylpyrazole-1-carboxamide

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The deaquation of two isostructural compounds of general formula $[M(HL)_2(H_2O)_2](NO_3)_2$ ($M=Co, Ni$, $HL=3,5$ -dimethyl-1H-pyrazole-1-carboxamide) is discussed in the view of their crystal and molecular structure. The compounds contain the same number and type of hydrogen bonds of the adjacent nitrate ions, only in the opposite orientation. On the basis of their deaquation pattern such a small difference may be detected, i.e., methods of thermal analysis are sensitive enough to show very small structural differences.

Keywords: Co(II) and Ni(II) complexes, crystal structure, deaquation, 3,5-dimethyl-1H-pyrazole-1-carboxamide

Introduction

Pyrazole derivatives and its transition metal complexes are in the focus of our research for some time [1, 2], due to their various and diverse potential applicability including pharmaceutical [3–6] and industrial employment [7, 8] as well as theoretical studies [9] of biochemical processes. The main aim of our studies is to understand how the reaction conditions determine the course of the complex formation in order to design compounds with tailored structure. To learn about the effects affecting the structure of new compounds, a most comprehensive characterization of the compounds is needed, including X-ray structure determination. To prepare compounds in the suitable form for structural analysis is not an easy task. In our previous paper [10] we have described the adoption of a well known analytical procedure, the so called method of precipitation from homogenous solution [11], to obtain complexes in the form of single crystals as well as to predict the possible reaction pathways and the composition of the most likely formed compound. In this work we tried to use the method to prepare the chloride equivalents of isostructural diaquabis(3,5-dimethyl-1H-pyrazole-1-carboxamidine- κ^2N,N')M dinitrates, $M=Co(II), Ni(II)$ [12]. In the reaction of metal salts with 3,5-dimethylpyrazole-1-carboxamidinium nitrate ($HL \cdot HNO_3$) the presence of a base is preferred in order to eliminate the blocking effect of HNO_3 which prevents the possible

coordination through the carboxamidine group. Using acetates of Co(II) and Ni(II) the acetate ion acts as a Brønsted base and nitrate complexes are formed due to the presence of the nitrate ion from HNO_3 . In this paper we describe the reaction of the ammin complexes of Co(II) and Ni(II) chloride with $HL \cdot HNO_3$. Instead of the expected chloride complexes $[M(HL)_2(H_2O)_2](NO_3)_2$ ($M=Co, Ni$) were obtained, i.e., the same compounds were formed as with corresponding acetates. The thermal desolvation mechanism is discussed on the basis of structural data.

Experimental

Preparation of the compounds

The salt-to-ligand ratio was 1:2. The corresponding metal chloride ($CoCl_2 \cdot 6H_2O, NiCl_2 \cdot 6H_2O, 0.5$ mmol) was dissolved in cc. ammonia (1 cm^3). To the solution solid ligand, $HL \cdot HNO_3$, was added (1 mmol). When $HL \cdot HNO_3$ was completely dissolved the reaction mixture was diluted with 4 cm^3 EtOH. The mixture was left for crystallization for 48 h. The orange colored cobalt (**I**) and the pink nickel (**II**) compounds were filtered off, washed with cold EtOH and air dried. Yields for **I** and **II**: 25 and 18%, respectively. The elemental analysis data refer to the formation of $[M(HL)_2(H_2O)_2](NO_3)_2$. **I**: %, (calcd.): C, 29.10 (29.08), H, 4.91 (4.89), N, 28.32 (28.27), **II**: C, 28.98 (29.10), H, 4.91 (4.89), N, 28.85 (28.29).

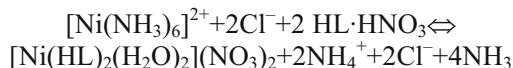
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Thermal analysis was performed using a DuPont 1090 TA system with sample masses of about 5 mg in argon atmosphere with a gas flow rate of 15 dm³ min⁻¹ and a heating rate of 10 K min⁻¹ in a platinum crucible, while DSC curves were recorded under the same conditions using an open aluminum pan sample holder and an empty pan as reference. EGD measurement was carried out by DuPont 916 TEA (Thermal Evolution Analyzer) instrument in flowing nitrogen and 8°C min⁻¹ heating rate.

Crystal structures were checked under identical conditions as described [12].

Results and discussion

The ligand, 3,5-dimethylpyrazole-1-carboxamidinium nitrate, may act as a bidentate NN ligand coordinating through the pyridine nitrogen, as is usual, and through N of carboxamidine NH₂- or NH-group. However, *HL* crystallizes with HNO₃, so its coordination ability is rather low, due to the blocking effect of the nitric acid. In the presence of a base HNO₃ may be eliminated, promoting thus the complex formation. In our former publication [12] we obtained nitrate complexes with *M*=Co(II) and Ni(II), [M(HL)₂(H₂O)₂](NO₃)₂, using M(II) acetates. As in the reaction the acetate ion was consumed to neutralize HNO₃ it was unlikely for the acetate ion to take part in the coordination. Also, the coordination ability of nitrate ion is usually low. Taking into account the coordination number of the metal ions, the formation of an aqua complex was very probable. On the contrary, chloride ion readily coordinates, often playing the role of a bridging atom. This time we tried to prepare chloride complexes with HL·HNO₃ in a form suitable for X-ray structure analysis. For this purpose ammin complexes of Co(II) and Ni(II) were applied, obtained by the dissolution of corresponding chlorides in cc. ammonia. The reaction of HL·HNO₃ with NiCl₂ in the presence of ammonia is given as



This means that HNO₃ is neutralized by evolved ammonia, avoiding thus its blocking of the carboxamidine-group and the ligand may coordinate in a bidentate NN mode. By this way two goals could be achieved: the neutralization of HNO₃ and a low initial metal ion concentration. Namely, ammonia acts as a base and a ligand at the same time. Its concentration determines the concentration of the metal ions through the corresponding stability constants. The low central ion concentration at the beginning of the reaction keeps the number of initial crystal nuclei also low, favoring thus the formation of single crys-

tals. The reaction is self-controlled: with the increasing concentration of the free ligand the concentration of the central ion is also increasing. In spite of the fact that in air with ammonia hexaammincobalt(III) ion is forming, with HL·HNO₃ cobalt(II) complex is obtained. We hoped for single crystals of the corresponding chlorides. However, the coordination preferences of the central ions towards water molecule compared to chloride ion favored the formation of [M(HL)₂(H₂O)₂](NO₃)₂, *i.e.*, the same compounds were obtained as with the corresponding acetates. Due to the different synthetical method the quality of the crystals obtained from the ammin complexes is much better. However, the yield is significantly lower 25% (**I**) and 18% (**II**) compared with 65% for each, using acetate salts.

Thermal decomposition

The structure of the compounds is described in detail in [12]. As they are isostructural, it was interesting to compare their thermal decomposition pattern. Namely, the decomposition of the isostructural compounds is usually very similar [13–20]. Sometimes, when it is not possible to determine the crystal and/or molecular structure of the compounds, similarity in the thermal decomposition patterns may refer to their isostructurality. However, a closer look at the thermal curves often refers to clearly distinguishable differences in decomposition of some isostructural compounds. We have found that the desolvation of isostructural Co(II) and Ni(II) complexes with *HL*'=3,5-dimethyl-1-(hydroxymethyl)-pyrazole [21], [CoCl(L')(EtOH)]₄ and [NiCl(L')(EtOH)]₄, is significantly different.

The thermal decomposition of **I** and **II** can be assessed only at the stage of the deaquation (dehydration). Namely, the decomposition of most of the nitrates at higher temperatures, even in an inert atmosphere, is exothermic, accompanied by uncontrollable oxidation processes, so it is meaningless to discuss the decomposition mechanism above the deaquation temperature. The TG-DTG curves in argon are presented in Fig. 1. The dehydration temperature is in the accordance with the water molecules being in the inner coordination sphere: it is near or higher in both compounds than the boiling point of water. The deaquation temperature for **I** is 355 K, while it is higher (415 K) for **II**. In addition, the anhydrous **I** is stable in about 50 K temperature range (the mean value of several runs, from different syntheses), while **II** decomposes further before the deaquation is accomplished. The mass loss (7.26%) in the case of **I** agrees with the experimentally determined one (7.3%). In **II** the experimentally determined mass loss (7.8%) is somewhat higher than the theoretical value (7.27%). In order to check if the higher mass loss of **II**

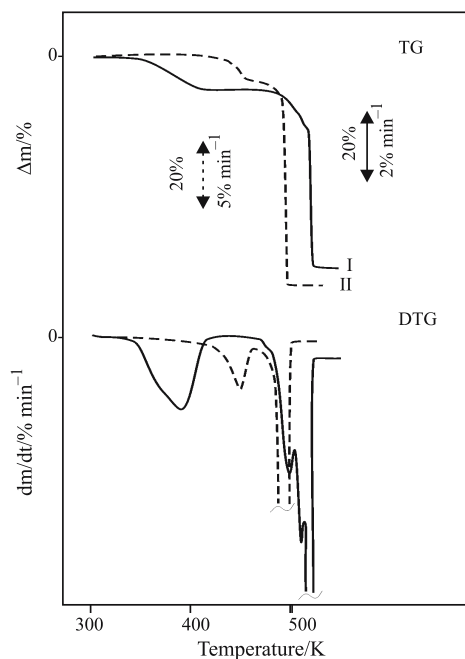


Fig. 1 TG-DTG curves of $[M(HL)_2(H_2O)_2](NO_3)_2$

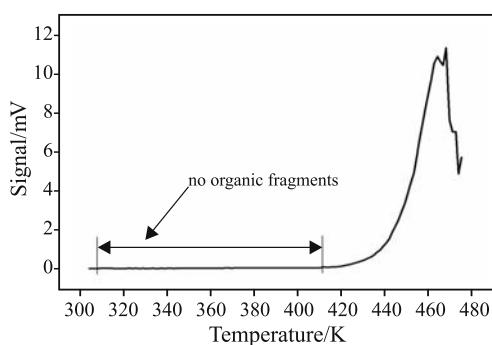


Fig. 2 EGD curve of $[Ni(HL)_2(H_2O)_2](NO_3)_2$

is due to some solvent occlusion, we have performed an EGD test (Fig. 2): there is no EtOH evaporation. However, this test does not exclude the presence of some occluded ammonia molecules. On the other hand, the desolvated **II** is not stable. It means that the somewhat higher mass loss of deaquation may be a consequence of the evolution of organic fragments from the next decomposition step. EGD curve is supporting the latter supposition (Fig. 2).

According to the reduced M-O(H₂O) distances in **I** and **II**, Co-O(H₂O), 2.1737 Å and Ni-O(H₂O), 2.152 Å, ($\Delta r=0.024$ Å, $\Delta r_{Co(II)-Ni(II)}=0.03$ Å [22]), the difference in M-O(H₂O) bond lengths is too small to explain the different deaquation temperatures. In addition, the asymmetrical DTG curves indicate that, in spite of the fact that M-O(H₂O) bond lengths in **I** and **II**, respectively, are equal, the departure of water molecules is not completely simultaneous. The difference in deaquation process is even better presented in Fig. 3. The derivatives of DSC curves emphasize the

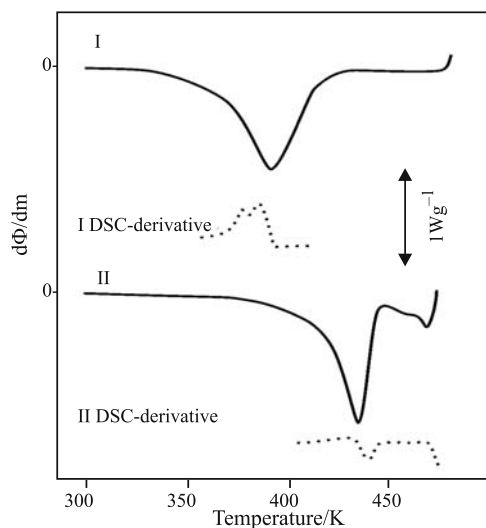


Fig. 3 DSC and DSC-derivative of **I** and **II**

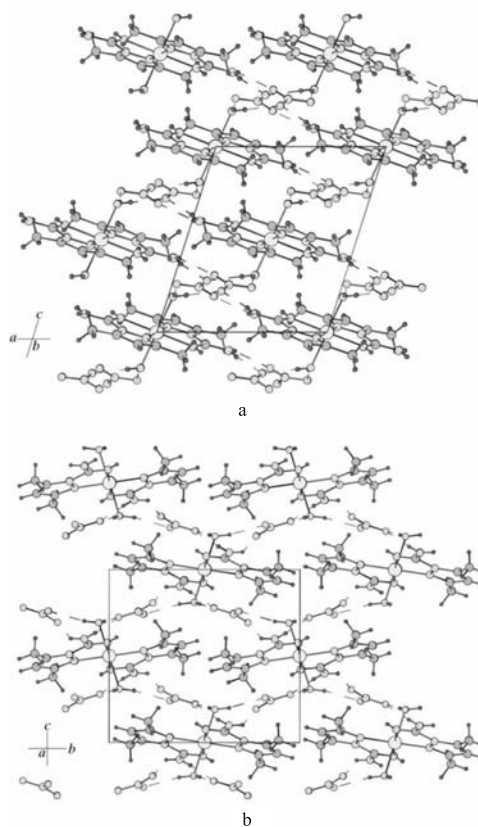


Fig. 4 Hydrogen-bonding schemes and views of packing for a – **I** and b – **II**

difference in H₂O evaporation in **I** and **II**. According to the crystal and molecular structural data, the packing diagrams of the compounds show that layers of cations are separated by layers of anions, and molecules lying parallel form layers of alternating orientations (Fig. 4). The most obvious difference between the two crystal structures is that despite the same number and types of hydrogen bonds of the adjacent nitrate ions, their orientation is opposite (Fig. 4). As a

conclusion, one may state that even such a small difference in the crystal structure of the isostructural compounds may be detected by thermal decomposition curves.

Conclusions

Using the method of precipitation from homogenous solution a good quality single crystals of $[M(HL)_2(H_2O)_2](NO_3)_2$ ($M=Co, Ni$, $HL=3,5$ -dimethyl-1H-pyrazole-1-carboxamide) were obtained from the ammin complexes made of Co(II) and Ni(II) chloride. However, instead of the expected chloride compounds, nitrates were formed. It means that the coordination preferences of the central ions are more explicit towards water molecule than towards chloride ion. The main difference in the crystal structure of the compounds is that the orientation of hydrogen bonds of the adjacent nitrate ions is opposite. This small difference in the crystal structure can be detected by the methods of thermal analysis.

Acknowledgements

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