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THE CLATHRATES OF TETRACYANOCOMPLEXES Ni(II) ISOLATED FROM STRONGLY AMMONIACAL MEDIA AND THEIR WATER CONTENTS

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ABSTRACT

The isolation of the tetracyano-nickelate clathrate compound from solutions of pH ≧ 9 range was studied in the case of the compound $Ni(NH_3)_mNi(CN)_4.nH_2O$. The purpose of the investigation was to examine mainly its different water content, forming its guest component and influencing on its thermal stability.

Helding the reaction media to pH ≧ 9 range, we prepared a solid coordinato-clathrate with very low quantities of the intercalated water, as is to be taken from the results of TG, DTA, DTG and IR spectra.

INTRODUCTION

The present investigation of the coordinato-clathrates /1/ of tetracyanocomplexes of Ni(II) with general formula $Ni(NH_3)_mNi(CN)_4.nH_2O$ isolated from ammoniacal media (pH ≧ 9) is in connection with the study of these compounds, isolated from the media with pH range 8-5 /2/. We found that the content of the guest component - in this case of the water - reflects in very sensible way the change of the pH value during the preparation. The content of water n = 1,9 was found after the isolation at pH 8, n = 2 at pH 7, n = 4 at pH 5. Thus by lowering the pH range, we may increase the amount of enclathrated water.

The order in the deliberation of gaseous products during their thermal decomposition by the combination of DSC an GC methods was found and specified. The compound prepared at pH 8 first lost the guest - the water and then the ammonia ligands /2/.

The water is situated in the layers of the lattice /3-5/. The distance of the layers in the intercalation compound is affected by the guest component content. Lowering the pH during the preparation to acidic range, the distance is increased and enables the sorption of more guest molecules.

The compound of the general formula $Ni(NH_3)_mNi(CN)_4.nG$ have various non-stoichiometric form. Just during their change from the stoichiometric to a non-stoichiometric form we found as possible to substitute the guest content by an appropriate organic

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compound /6/. The originally intercalated species (water or aromatic compound) was totally or partially substitued.

We found reversible sorption of the water also in IR spectra /2/. The samples of $Ni(NH_3)_2Ni(CN)_4.1,9H_2O$ and $Ni(NH_3)_2Ni(CN)_4.4H_2O$ after heating to 190°C (in normal thermal decomposition the water content is lost) in measured IR spectra (KBr disc) showed again the presence of the resorbed water.

As very interesting results we found the interaction of the $M(NH_3)_mM'(CN)_4.nH_2O$ compounds (M = Ni, Cu, M'= Ni) with different organic compounds, acting as auxiliary modifying solvents /7/. The water, methanol, hexan, cyclohexane did'nt affect their IR spectra and diphractographic patterns, but ameliorated their properties, when we used them as stationary phase in GC. Pyridine /7/ or dioxane /8/ substituted not only the ammonia ligands but also the original guest and the distance of layers was changed, equally their selectivity toward the mixtures of several organic compounds increased.

I.Uemasu and I.Iwamoto /9/ studied the hydratation reactions of $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$ after its suspension in aqueous media. Reacting with H_2O or diluted HNO_3 the compound substituted not only its benzene content, but also the ammonia ligands.

MEASURING METHODS

The preparation of the clathrates of tetracyanocomplexes Ni(II) of general formula $Ni(NH_3)_mNi(CN)_4.nH_2O$ was analogous as the previously described /2/ using the media of pH 5-8. By mixing solutions of Ni II (6g $NiSO_4.7H_2O$ in 25ml H_2O) and KCN (3g KCN in 25ml H_2O), $Ni(CN)_2$ was prepared, which was immediately dissolved by adding 28-30 ml NH_4OH (25%). The resultant solution was simultaneously cooled and mixed with acetic acid (60%) to lower the pH value step by step to 11, 10, 9 and a precipitate was obtained. Each precipitate was filtered and then washed with ethyl alcohol, ether and kept in a dessicator over silica gel.

For better distinguish the formation of the clathrate during the preparation by continualy changing the pH range we determined the titration curve of the $Ni(NH_3)_mNi(CN)_4$ and acetic acid (60%). We used pH meter (Radelkis OP 102) with glass and calomel electrodes, automatic byret (OP 930) and recorder (TZ 4100 Laboratórní přístroje Praha).

The composition of compounds was checked by elemental analyses (Hewlett Packard CHN Model 185) and IR spectra (Perkin-Elmer Model 577, KBr disc technique).

All TG, DTG, and DTA analyses of prepared compounds were measured up to 600°C in air (Derivatograph MOM OD 102, Paulik-Paulik - Erdey), with equal parameters (weight of sample 200 mg; sensivities: TG, 200 mg; DTA, 1/5, DTG, 1/5; heating rate, $6^{o}min^{-1}$; reference material, Al_2O_3).

RESULTS AND DISCUSSION

The isolation made from the ammoniacal media (pH>9) showed that in this case the minimal quantity of water guest was achieved. The range of pH about pH>9 is not very favorable for the isolation. In contrary the pH range about 8-5 was very convenient, the compound may be well and in a sufficient yield isolated with an adequate amount of water sorbed as guest. The low yield of samples isolated at pH>9 is in accordance with the course of their titration curves, mainly at pH 11.

The IR spectra showed the identity of the samples. By comparison of the IR spectra of samples isolated at pH 8, 9, 10 and 11 we could see the decreasing content of water, mainly in its frequencies at 1650-1350 and 3300-3200 cm^{-1}.

Studying the thermogravimetric results (TG, DTG and DTA), we found that the thermal decomposition of samples is in three steps and it is analogous as after isolation from neutral or acidic media. In two endothermic processes we can distringuish the loss of water and ammonia and in the exothermic process the decomposition of cyanides (Fig.1). For the comparison we show on fig.1 also the curves of the sample isolated at pH 7 from the solution. The loss of the intercalated species - water-begins at about 50°C. The compound stayed without change after standing during six months - in the TG curves.

The quantities of the intercalated H_2O are low: in the case of the sample isolated at pH 9 about 0,4-0,5, at pH 10 $n \cong 0,3$ and pH 11 $n \cong 0,2$.

The samples of coordinatoclathrates isolated at different pH are not only with different quantities of sorbed water, but they may be finely distiguished in colouring. The samples isolated from media pH 8-5 are lightly bleu, these from strongly ammoniacal media are sooner lightly violet.

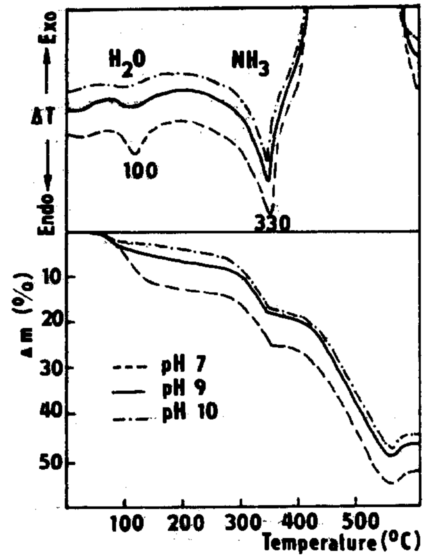

Fig. 1. TG and DTA curves of $Ni(NH_3)_m(CN)_4.nH_2O$

CONCLUSION

When we made a deviation from the experimental conditions we observed different amount of the sorbed water in the prepared compounds. Changing the conditions by lowering the pH (also into the more acidic regions) in reaction media, the quantity of intercalated water is increasing. In strongly ammoniacal media the quantity of intercalated water are rather low (n less as unity), but the compound stays as a clathrate (n > 0). Only if n = 0, the compound has not areas for the enclosure of the guest at all.

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