Thermochimica Acta, 92 (1985) 727-730
Elsevier Science Publishers B.V., Amsterdam

EFFECTS OF SURROUNDINGS IN NiNi/CN/$_4$ AND ITS THERMAL STABILITY

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ABSTRACT

The effects of surroundings on the simple tetracyanocomplex MM'/CN/$_4$ show changes in the thermal stability of prepared compound. As surroundings were succesively chosen: several couples of metal ions M,M', different kind and number of ligands, but also the molecules of water or some aromatic compounds capable to form in different quantities the enclathrated guest component in the layered structure of the tetracynocomplex clathrate having at all the formula: MB$_4$M'/CN/$_4$.nG/where B is oxigene or nitrogene containig base, G is aromatic compound or water/. The NiNi/CN/$_4$ in its hydrated form was the as basic observed compound and it was succesively increased up to the Ni/NH$_3$/$_2$Ni/CN/$_4$.nC$_6$H$_5$OH and this one was investigated also after its longer static or dynamic contact with further aromatic compound:benzene.

INTRODUCTION

The fundamental unit of the clathrate of tetracyanocomplexes is MM'/CN/$_4$, where M,M'are different or the same metals. The compound alone is not often studied, it is used as starting compound for further synthesis. Which properties the isolated compound alone exhibits, for example NiNi/CN/$_4$ and resp. which changes it undergoes after its interaction with other compounds-mainly its thermal stability, this was interesting for us when we compared the results of TA with results of IR spectra, difractographic and magnetic measurements.

MEASURING METHODS

Preparation of NiNi/CN/$_4$.7 H$_2$O is relatively simple. It is published also in /1/. We started with Ni/NO$_3$/$_2$ and KCN and further again with Ni/NO$_3$/$_2$. Voluminous ligthly blue precipitate was after isolation and drying identified as NiNi/CN/$_4$. 7 H$_2$O (1). One part of them was used for further synthesis. The tetracyanocomplex was gradually diluted in aqueous ammonia, cooled and by mixing and after modifying the reaction media to p$_H$ 9,5 phenol dissolved in water was added. As product we gained compound (2) Ni/NH$_3$/$_2$Ni/CN/$_4$. 0,24 C$_6$H$_5$OH.The problem of actual p$_H$ at synthesis of analogous clathrates is treated in /2/.

Analysis were made by CHN /Hewlett Packard 185/. The starting

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Proceedings of ICTA 85, Bratislava

compound, products and intermediates were studied /3/ by difractometric /Mikrometa 2,Chirana/ and spectrometric /IR Specord 75 Carl Zeiss, Jena/ measurements in KBr discs.

Thermal analysis was made in air by Derivatograph /OD Paulik,Paulik, Erdey, MOM Budapest/ at equal parameters /100 mg; DTA, DTG 1/5; T:500°C; rate of heating 5,10°C/min/.

Sorption experiments were made after isolation and identification of the compounds (1) and (2). The static experiments were performed at 25°C by 10 days long acting - sample S, the dynamic in Soxhlett extractor-sample D /about b.p. of C_6H_6/.

Further we verified the conserved layered structure of the coordinatoclathrate (2) at temperatures enabling the deliberation of the phenol-guest between 70 and 250°C. Before ending this interval at 240°C/n $\rightarrow$ 0/ its structure was still conserved and capable of further sorption. The heating was made /5°C/min/ in Derivatograph and the product-sample D was before the dynamic sorption experiments with benzene identified. The isomorphous forms before and after difractographic measurements showed /3/ the partially deliberated areas /4/ after the loss of phenol were occupied with benzene /see also Table 2/.

RESULTS AND DISCUSSION

Thermal decomposition with results is in Table 1 and 2 summarized. The thermal stability of the tetracyanocomplex by its interaction with benzene was changed. The content of the enclathrated species are non-stoichiometric /5/. The adsorbed matter was present also in little quantities, always after the accessibility ot the interlayer areas.

The presence of the paramagnetic Ni ion /6,7/ was studied /3/ in measurements of the magnetic susceptibilities /by method Faraday/. Although the Ni/II/ ion is gradually surrounded not only by ligands, but also by enclathrated species and sometimes also by two species of the enclathrated-in the sense of the host lattice intercalated guest molecules-all compounds showed their paramagnetic character. The ligands and guest do not compensate the paramagnetismus of Ni/II/ but we could see a slightly changed values - always after the type and amount of surrounding components /3/ in the molecule. Our results satisfied-although in paper /2/ the investigated product was less complicated as our product gained after the partial

Table 1. Thermal decomposition of (1) and the product of sorption experiments with C_6H_6 /3/.

	T /°C/ Δm /%/ loss of:				
$NiNi/CN/_4 \cdot 7H_2O$ (1)	40-120 26,5 4,96 H_2O	120-170 10,5 1,96 H_2O	170-240 3	240-370 21 4 CN	380-506 39 rest:ox.
$NiNi/CN/_4 \cdot 2,6H_2O \cdot$ $\cdot 0,3C_6H_6$ (S)	30-80 11 1,5 H_2O	80-115 9,5 0,38 C_6H_6	115-140 8,5 1,1 H_2O	240-350 28 CN	350-500 43 rest:ox.
$NiNi/CN/_4 \cdot 2,6H_2O \cdot$ $\cdot 0,36C_6H_6$ (D)	40-110 14 2,6 H_2O	110-175 10 0,36 C_6H_6		240-350 26,5 4 CN	350-500 50,5 rest:ox.

Table 2. Thermal decomposition of (2) and the product of sorption experiments with C_6H_6 /3/.

	T /°C/ Δm /%/ loss of:				
$Ni/NH_3/_2Ni/CN/_4 \cdot$ $\cdot 0,24C_6H_5OH$ (2)	40-70 6 $1NH_3$	70-250 14 $1NH_3$ 0,24ph		270-420 34 4CN	420-500 46 rest:ox.
$Ni/NH_3/_2Ni/CN/_4 \cdot$ $\cdot 0,19C_6H_5OH \cdot$ $\cdot 0,2C_6H_6$ (S)	60-110 4 $0,2C_6H_6$	210-250 3,99 0,19ph	245-350 8,1 $1,8NH_3$	380-440 1,2 0,3 NH_3	410-520 30,0 4CN
$Ni/NH_3/_2Ni/CN/_4 \cdot$ $\cdot 0,27C_6H_5OH \cdot$ $\cdot 0,14C_6H_6$ (D)	63-110 4 $0,14C_6H_6$	110-180 4,5 $1NH_3$	180-250 9,5 $1NH_3$ 0,2ph	250-450 39 CN	43 rest:ox.
$Ni/NH_3/_2Ni/CN/_4 \cdot$ $\cdot 0,2C_6H_5OH \cdot$ $\cdot 0,2C_6H_6$ (P.D.)	32-85 7,5 $1,3NH_3$	85-145 5,5 $0,2C_6H_6$	145-230 6,5 0,2ph	230-250 2 $0,3NH_3$	250-110 36,5 4CN

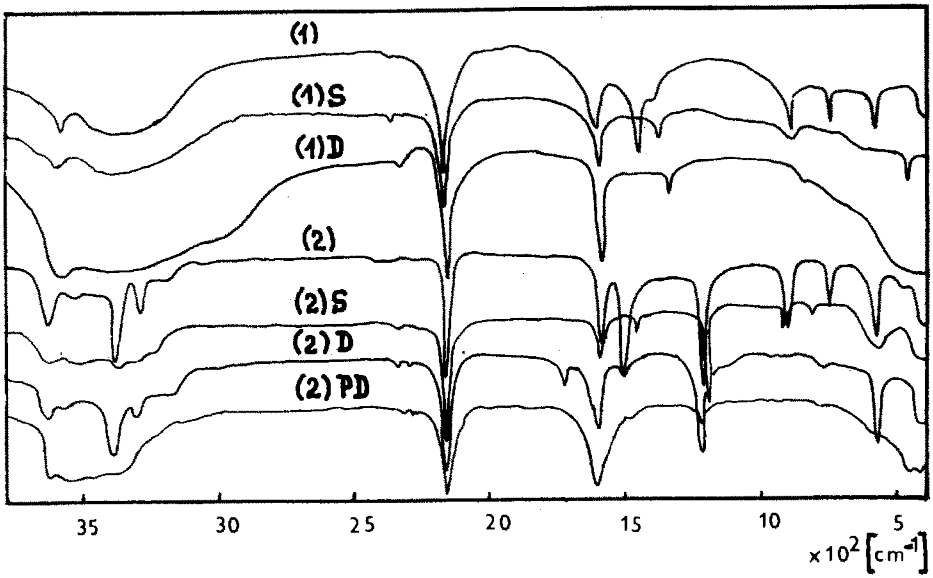
S-static; D-dynamic sorption; P.D.-part.destructed; ph-phenol decomposition of (2) and after its interaction with further sorbent.

CONCLUSIONS

The influence of the surroundings on the fundamental MM'/CN/$_4$ is evident in TA, equally in the sorption, resorption resp. substitution of the guest, also in IR spectra, difractographic and magnetic measurements.

The bond strength Ni-CN in the simple tetracyanocomplex is affected by the presence and numbers of individual components in the gradually increasing molecule and even more after a new guest. It is presented in the shifts of the temperatures of decompositions of each sample /Table 1,2/ and in their aproppriate DTA Max and in IR spectra /Figure 1/

Fig.1: IR spectra of original compounds and after the sorption.



With incresing surroundings the bond strength is changed in IR spectra too. The bond strength Ni-CN and M-C is decreasing after the partial decomposition of (2) and it is without $\nu_{s\ NH}$ and with weakened ν_{M-C} after its contact with benzene.

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