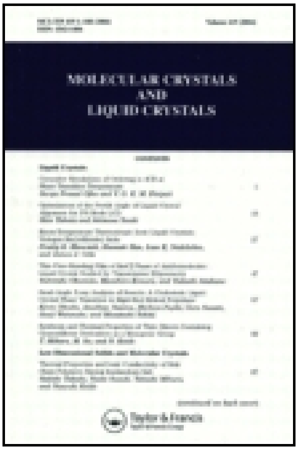

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E. Stumpp [a] & C. Ehrhardt [a]

[a] Institut fur Anorganische und Analytische Chemie der TU Clausthal Paul-Ernst-Strasse 4, D-38670, Clausthal-Zellerfeld, Germany

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REACTION OF METAL CHLORIDE GRAPHITE INTERCALATION COMPOUNDS WITH AMMONIA

E. STUMPP AND C. EHRHARDT
Institut für Anorganische und Analytische Chemie der TU Clausthal
Paul-Ernst-Strasse 4, D-38670 Clausthal-Zellerfeld, Germany

Abstract The uptake of ammonia by copper chloride graphite intercalation compounds was studied. The products obtained can be represented by the formula $\{xC\}CuCl_2{\cdot}nNH_3$. They are regarded to be occlusion complexes. The thermal decomposition of these complexes has been studied and compared with those of ammine complexes of $CuCl_2$. The techniques used were thermogravimetric analysis supported by chemical analysis and X-ray diffraction. When heated in a slow stream of ammonia or nitrogen, ammonia is lost in steps, which are better defined when the decomposition takes place in ammonia. The decomposition finally leads to the formation of CuCl mixed with graphite.

INTRODUCTION

Some metal chloride graphite intercalation compounds (GICs) are fairly stable in water although the starting metal chlorides are highly soluble in water. The reason for this inertness is still unclear. In contrast, certain GICs with transition metal chlorides react readily with liquid or gaseous ammonia. It seems that the capability of a transition metal chloride GIC to take up ammonia depends on the sample preparation. Rüdorff and Schulz [1] reported that iron chloride graphite was found to react readily with liquid ammonia but very slowly with gaseous ammonia. The amount of ammonia uptake was 6 mole NH_3 per mol $FeCl_3$. While Pitts and Lyon [2] could not find any evidence for a reaction of $CoCl_2$-graphite with ammonia, Touzain et al. [3] found that a reaction took place. We observed that samples of $CoCl_2$-graphite which were washed with water showed reactivity only in liquid ammonia [4].

As reported by Touzain et al. [3,5] the systems metal chloride GIC/NH_3 can be used to store thermal energy. These authors showed that upon reaction of $MnCl_2$-GIC and $MgCl_2$-GIC, respectively, with ammonia the GICs were decomposed. Since the X-ray diffractograms show the reflections of $Mn[NH_3]_6$ Cl_2 and $Mg[NH_3]_6Cl_2$, respectively, these ammines are not intercalated between the graphene sheets but entrapped in the graphite matrix. The ammines could be removed only partially from the products by washing with water. Touzain et al. [5] call the products "inclusion compounds" to distinguish them from genuine intercalation compounds.

This paper describes a study of the uptake and loss of ammonia by $CuCl_2$-graphite by means of quasi-isothermal thermogravimetry supported by chemical analysis.

EXPERIMENTAL

Natural flake graphite (Kropfmühl, Bavaria) of particle size ca. 0.5 mm was used. C_5CuCl_2 (stage 1) was prepared by heating anhydrous $CuCl_2$ with graphite in a sealed tube, filled with gaseous chlorine, at 500 °C for 5 days. To obtain a stage 2 sample the stage 1 compound was heated in a stream of chlorine at 500 °C for 3 days. It had the composition $C_{7.4}CuCl_2$. $Cu[NH_3]_6\,Cl_2$ was prepared by the action of liquid ammonia on anhydrous $CuCl_2$. Excess ammonia was allowed to evaporate, leaving the hexaammine. The samples of $CuCl_2$-GIC were treated in the same manner.

Thermal gravimetric analyses (TGA) were performed with a magnetic suspension balance (Sartorius, Göttingen, model 2401). In this balance the mass recording part is separated from the sample compartment. The samples were heated in a steady flow (0.2 L/min) of dry nitrogen and ammonia, respectively. The TGA were run nearly isothermal by adjusting the heating rate to the mass loss of the sample, regulated by a computer. With this technique the exfoliation of the GIC samples on heating can be almost completely suppressed.

RESULTS AND DISCUSSION

The TGA curves for $Cu[NH_3]_6Cl_2$ (sample I) in nitrogen and ammonia, respectively, are shown in Figure 1. The decomposition occurs in a well defined three-step mass loss. In order to identify the intermediate products a second experiment was performed in which the intermediates were isolated at the desired temperature and analysed. The mass loss in the TGA agreed fairly well with the analytic data. Both curves show some slight mass loss at a temperature just above ambient. If the starting complex is formulated as $CuCl_2 \cdot nNH_3$ with $n = 6$, this mass loss corresponds to a decrease of n from 6 to 5. In nitrogen (curve 2) there is a step at 53 °C, followed by a further one at 86 °C. Both steps occur also in ammonia (curve 1) but are shifted to higher temperatures. At point B the value of n was found to be 3.4. The long plateaux C correspond to the complex $Cu[NH_3]_2Cl_2$. It decomposes at 235 °C in nitrogen and in at 295 °C ammonia to form CuCl.

The ammines of copper chloride with n = 6, 3.3 and 2 were formerly observed by Biltz et al. [6] during the isothermal decomposition of the complex obtained by reaction of $CuCl_2$ with liquid ammonia. As would be expected the thermal stability of the intermediates is higher in ammonia than in nitrogen.

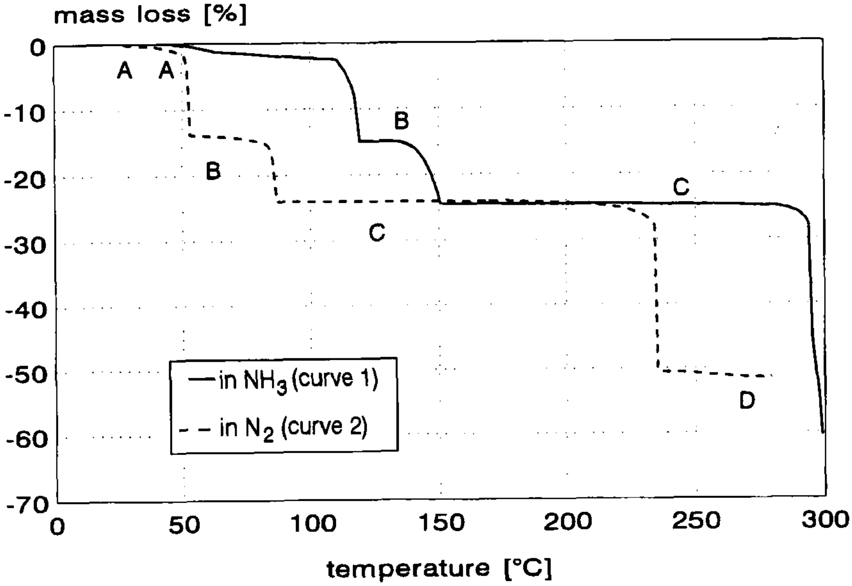

FIGURE 1. TGA curves for $CuCl_2 \cdot nNH_3$. Values for n at marked points: A (n = 6), B (n = 3.4), C (n = 2).

The X-ray diffractogram of the samples of $Cu[NH_3]_6Cl_2$ used in this study could be indexed with the unit cell dimensions a = 10.27 Å and c = 9.42 Å reported by Elliot et al [7].

Two samples of C_5CuCl_2 (stage 1) were treated with ammonia. To the GIC-samples ammonia was distilled at ca. -50 °C and then the mixtures were allowed to warm up to room temperature. This procedure yielded products with a ratio NH_3:Cu = 5.9 (sample **IIa**), and 5.7 (sample **IIb**), respectively. Under the microscope small blue crystals could be detected beside the black graphite bulk. By washing with water only a small part of the copper complex was removed. The residue gave an X-ray pattern which showed the same reflections as $Cu[NH_3]_6Cl_2$. Also the 002 reflex of graphite but no reflections of the starting $CuCl_2$-GIC were observed.

In accordance with the results of Touzain et al. [5] we conclude, that the uptake of ammonia by $CuCl_2$-graphite leads to decomposition of the GIC. The ammine complex is assumed to be entrapped in holes of the graphite matrix which are formed during decomposition. Since the term "inclusion compound" is used in the chemical literature for well defined chemical substances with, as a rule, stoichiometric composition we propose the term "occlusion complex" for the systems graphite/metal chloride/ammonia. To discriminate such a system from a genuine GIC we favor the formula $\{5C\}\ CuCl_2 \cdot nNH_3$ for the product obtained by treating C_5CuCl_2 with ammonia.

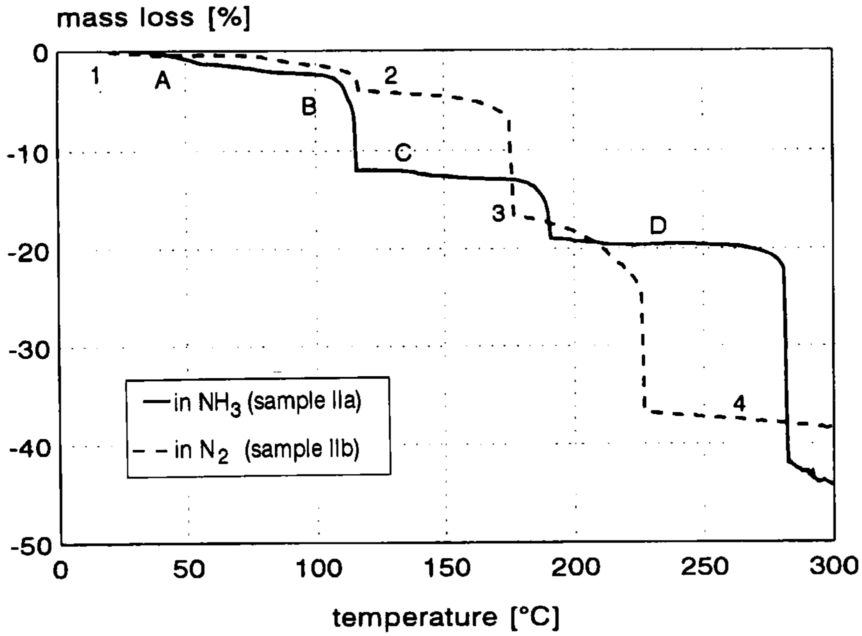

FIGURE 2. TGA curves for the decomposition of {5C}$CuCl_2 \cdot 5.9NH_3$ in ammonia and of.{5C}$CuCl_2 \cdot 5.7NH_3$ in nitrogen.

The TGA curves for heating the sample **IIa** in ammonia and sample **IIb** in nitrogen are shown in Figure 2. The TGA curve **IIa** exhibits a three-step mass loss up to about 270 °C. The end product of the degradation was identified by chemical analysis to be CuCl. The points marked in the TGA curve correspond with the following ratios: n = NH_3:$CuCl_2$: B, n = 5.2; C, n = 3.3; D n = 2.1. Whereas the decomposition to the product with n = 3.3 takes place at the same temperature as in the TGA curve for $Cu[NH_3]_6Cl_2$ (Figure 1)), the further mass loss of **IIa** occurs at an appreciably higher temperature. The TGA curve of (**IIb**) is different from that of (**I**) and also from that of (**IIa**). The corresponding n-values are: at point 1, n = 5.7; at 2, n = 5.0, at 3, n = 2.9. The sloping plateau beginning at 3 indicates a continuous decomposition with no well defined intermediates.

In the same manner as described above for C_5CuCl_2 two samples of a stage 2 $CuCl_2$-GIC were treated with ammonia. The compositions were {7.4C}$CuCl_2 \cdot 6.6NH_3$ (sample **IIIa**) and {7.4C}$CuCl_2 \cdot 6.2NH_3$ (sample **IIIb**), respectively. The TGA curves for these samples are displayed in Figure 3. (**IIIa**) was decomposed in ammonia and (**IIIb**) in nitrogen. The TGA curve for (**IIIa**) resembles that for (**IIa**). The n-values are: at A, n = 6.6; at B, 6.0; at C, n = 3.8; at D, n = 3.0. The slight mass loss with increasing temperature in the region C indicates the presence of a mixed phase.

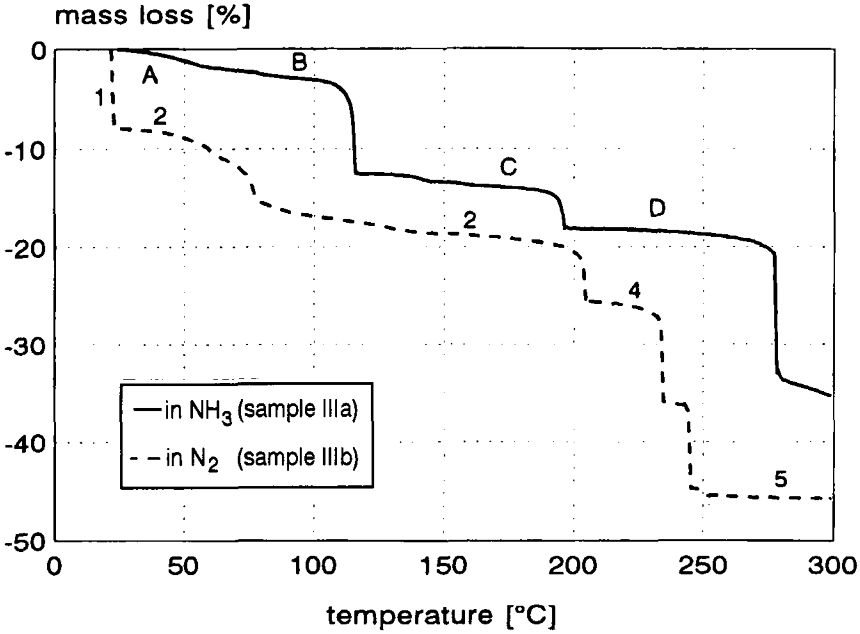

FIGURE 3. TGA curves for the decomposition of {7.4C}$CuCl_2 \cdot 6.6NH_3$ in ammonia and of {7.4C}$CuCl_2 \cdot 6.2NH_3$ in nitrogen.

The decomposition curve for (**IIIb**) is notably different from that for (**IIb**). In the sloping regions 2 and 3 there is a gradual decomposition of more than one species. The n-values corresponding to the marked points are: at 1, $n = 6.2$; at 2, $n = 5.0$; at 3 $n = 4.1$; at 4, $n = 2.5$. The residue at 5 was found to be CuCl.

To investigate whether the decomposition steps are reproducible, experiments with repeated runs were performed. The sample {5C}$CuCl_2 \cdot 5.9NH_3$ was heated up in an ammonia stream to the point at which the sample is decomposed to {5C}$CuCl_2 \cdot 2.1NH_3$ (Figure 4). Then the sample was allowed to cool in ammonia gas to room temperature. As can be concluded from Figure 3 this procedure yielded again the product {5C}$CuCl_2 \cdot 5.9NH_3$. Then a TGA was started again. In the second run the first step occurs at about the same temperature as in the first run but beyond that temperature there is a steady mass loss. The second TGA trace reaches the curve of the first run at the point corresponding to a sample of the composition {5C}$CuCl_2 \cdot 2.1NH_3$. The same procedure was performed starting with {7.4C}$CuCl_2 \cdot 6.6NH_3$.

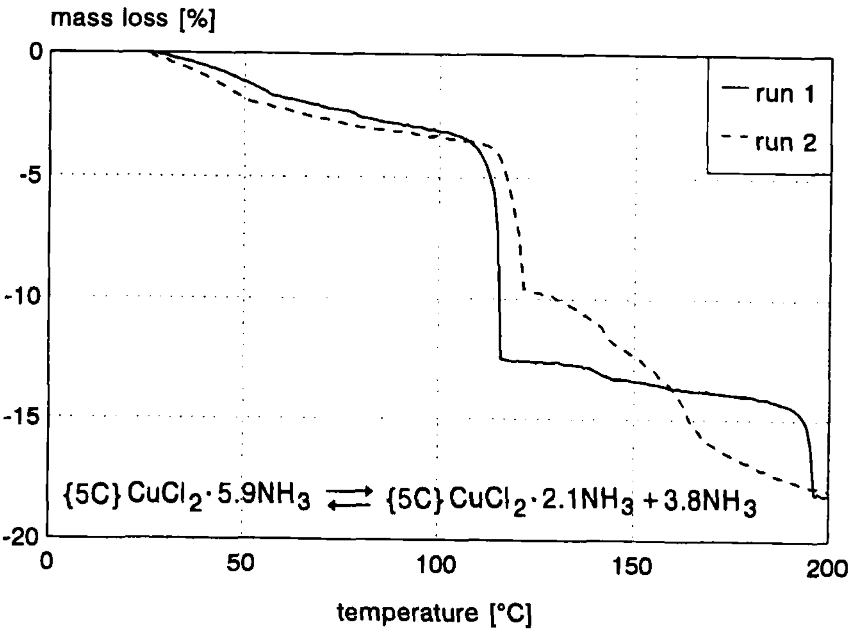

FIGURE 4. TGA curve for decomposition of {5C}$CuCl_2 \cdot 5.9NH_3$ in ammonia to {5C}$CuCl_2 \cdot 2.1NH_3$ (run 1). Regeneration of {5C}$CuCl_2 \cdot 5.9NH_3$ by uptake of ammonia upon cooling. Then start of a second TGA (run 2).

CONCLUSIONS

$CuCl_2$-graphite has been found able to uptake ammonia. There is no evidence in the X-ray results that the product formed is a GIC. On the contrary, this reaction leads to a decomposed GIC with entrapped species of ammine complexes of $CuCl_2$. The results of TGA studies support this conclusion. The apparent higher thermal stability of the entrapped ammine complexes in the lower temperature region is supposed to be caused by kinetic effects or by the fact that the vapor pressure of ammonia over the species entrapped in holes in the graphite matrix can attain higher values than atmospheric pressure.

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