3692 © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 3692—3694 (1990) [Vol. 63, No. 12

Thermal Decomposition of Copper(II) Polyamine Complexes

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(Received August 6, 1990)

Synopsis. The thermal decomposition of the complexes of copper(II) chloride and sulfate with polyamines has been investigated in detail by thermal analysis, X-ray powder diffraction and ESR spectroscopy. It has been revealed that the chloride complexes decompose to copper metal and carbonaceous product in nitrogen and to copper(I) chloride in air, and the sulfate complexes to copper(I) sulfide and carbonaceous product in nitrogen and to copper(II) oxide in air.

The thermal decomposition of tetraamminecopper(II) sulfate[1] has been studied extensively in relation to that of copper(II) sulfate pentahydrate. Little is known, however, about the pyrolysis of its ethylenediamine[2] and other polyamine complexes.

During the ESR study of alumina doped with copper(II) polyamine chlorides[3] we found an unexpected fact that these complexes exhibit a strong, sharp endothermic peak about 250 °C in the DTA curves, as if it were due to melting of the complexes. The purpose of this study is to report that these polyamine complexes show new features in thermal decomposition. A comparison of the pyrolytic behavior between the chloride and sulfate is also a theme of this investigation. The production of copper metal and of copper(I) sulfide through the thermal decomposition of copper(II) polyamine complexes in a nitrogen atmosphere has not yet been clarified.

Experimental

N,N′-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet; bp 266—267 °C; Kanto Chemical Co., Ltd) and 1,4,8,11-tetraazacyclotetradecane (cyclam; mp 184—186 °C; Aldrich Chemical Co., Ltd.) were used without further purification. Commercial grade *N,N′*-bis(3-aminopropyl)ethylenediamine (3,2,3-tet; Aldrich Chemical Co., Ltd.) was distilled and the fraction at 150—160 °C/5 mm Hg (1 mmHg= 133.322 Pa) was collected. Copper(II) chloride dihydrate and sulfate pentahydrate, and other chemicals were of reagent grade from Kanto Chemical Co., Ltd. and used as received.

A published procedure[4] was modified for the preparation of the chloride and sulfate complexes of copper(II) polyamines by the reaction of the parent copper salts with a small excess of each polyamine. Found: C, 26.32; H, 7.47; N, 17.53. Calcd for $\mathrm{Cu(2,3,2\text{-}tet)Cl_2\cdot H_2O}$: C, 26.88; H, 7.09; N, 17.92 %. Found: C, 29.47; H, 7.76; N, 17.40. Calcd for $\mathrm{Cu(3,2,3\text{-}tet)Cl_2\cdot H_2O}$: C, 29.41; H, 7.40; N, 17.15 %. Found: C, 22.18; H, 6.73; N, 14.70. Calcd for $\mathrm{Cu(2,3,2\text{-}tet)SO_4\cdot 3H_2O}$: C, 22.49; H, 7.01; N, 14.98 %. Found: C, 20.08; H, 7.01; N, 11.36. Calcd for $\mathrm{Cu(3,2,3\text{-}tet)SO_4\cdot 6H_2O}$: C, 19.9; H, 7.3; N, 11.6 %.

Thermal analyses (TG and DTA) were recorded on a Shinku-Riko TGD-1500 RH-P differential thermobalance at a constant heating rate of 5 °C min^{-1} under the dynamic atmospheres of air and nitrogen. ESR measurements were made on a JEOL JES-FE1XG ESR spectrometer (X-band) at room temperature and at 77 K. In order to record for thermal decomposition products the complexes were heated in an ESR tube while flowing air or nitrogen; the tube was sealed. X-Ray powder diffraction was carried out on a Rigaku Geigerflex D-3F diffractometer using Ni-filtered Cu $K\alpha$ radiation.

Results and Discussion

The TG and DTA curves of $\mathrm{Cu(3,2,3\text{-}tet)Cl_2}$ are given in Fig. 1. The TG curve in nitrogen (Fig. 1A) shows weight losses in three steps: the first, being about 5%, is in good agreement with the calculated one to form an anhydrous complex upon losing one water molecule; the second, being about 60% and resulting in a break in the curve at 440 °C, is the decomposition of the ligand to some volatile components and carbonaceous matter (cracking and carbonization); the last, being a gradual loss of about 2% and continuing up to 800 °C, is due to a graphitization of the products. Since the residue at 800 °C contains copper metal and carbon, as described later, and the content of copper is calculated to be 19.4% of the original complex; about one-third of the residue by weight (9.6% in the TG curve) is carbon. In the DTA curve (Fig. 1C) a weak endotherm at 150 °C, and a strong and sharp one at 230 °C followed by two endothermic reactions at 310 and 410 °C correspond to the first two steps in the TG curve, respectively. The endothermic reaction at 230 °C begins at 210 °C and terminates at 250 °C. This seems to represent the

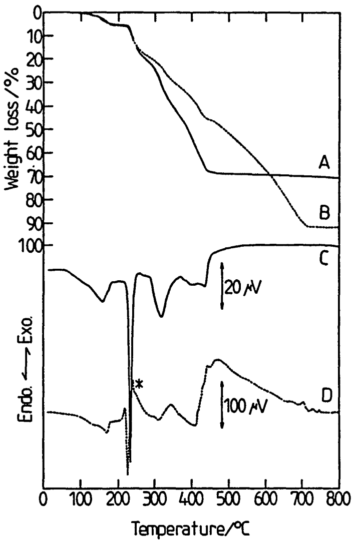

Fig. 1. TG and DTA curves of $\mathrm{Cu(3,2,3\text{-}tet)Cl_2}$ under atmospheres of nitrogen and air.
——, in nitrogen; ----, in air. Sample weight: 50 mg. Heating rate: 5 °C min^{-1}. *, see in the text.

melting of the complex. If this is the case, the reaction should be reversible. When the sample, which had been heated at 230 °C, was again heated from room temperature to 300 °C, no sharp endothermic peak around 230 °C could be found. Although this reaction takes place with violence in a very narrow temperature range, the weight loss due to the reaction is less than one-sixth of the total weight loss in the second step of the TG curve. Therefore, the significant decrease in temperature due to the endotherm at 230 °C may be attributable to the formation of a lower valent copper, i.e., Cu^+ and Cu^0, caused by an electron transfer between copper and ligand nitrogen atoms. The complex changed from deep violet powder to a light brown and a viscous liquid between 210 and 250 °C; immediately, a red-tinged lustrous deposit was recognized to form and was identified as being copper metal by X-ray diffraction, as would be expected (Fig. 3). With increasing temperature, an intensity decrease of the ESR signal due to divalent copper and, finally, its disappearance were also observed for pyrolyzed products. Above 300 °C the viscous liquid turned into a dark-brown solid substance, although the copper metal remained unaltered. As a result, it is presumed that $Cu(3,2,3\text{-tet})Cl_2$ decomposes to copper metal and a partially decomposed 3,2,3-tet molecule upon heating up to 250 °C. Once the dissociation of the complex begins, the polyamine moiety left alone should burst out decomposing. That the direct formation of copper metal does not take place via copper(II) chloride is certain, since its dihydrate decomposes to anhydrous copper(I) chloride upon heating above 470 °C under an atmosphere of argon and in vacuo.[6] Three chloride complexes decompose in a similar manner under an atmosphere of nitrogen. It has been observed that the temperature of the second endothermic peak in the DTA curve becomes high in the order of increasing stability of the complex (Table 1).

The TG and DTA curves of $Cu(3,2,3\text{-tet})Cl_2$ in air (Figs. 1B and D) have some important features which are different from those in nitrogen (Figs. 1A and C): there are two strong exotherms in the DTA curve (the one at 240 °C (* in Fig. 1D) overlapped with a sharp endothermic peak at 220 °C, the other ranging widely in temperature from 420 to 700 °C); a residue of about 7% at 800 °C is appreciably small (the expected value for copper(II) oxide, if formed, will be 24.3%). The DTA curves up to 420 °C in air and in nitrogen have an analogous shape, except for an exothermic reaction at 240 °C in air. This reaction at 240 °C, in which copper metal is deposited on the bottom of a platinum crucible (as detected by X-ray diffraction), is attributed to the combustion of evolved gaseous components from the ligand. The product above 700 °C was not copper(II) oxide, but copper(I) chloride (Fig. 3), con-

Table 1. Stability Constants of the Copper(II) Polyamine Chlorides, and Their TG and DTA Results in Nitrogen

Complex	Stability constant[a)]	TG	DTA	
		Weight loss in the first step/%	I[b)]/°C Peak[c)]	II[b)]/°C Peak[c)]
$Cu(2,3,2\text{-tet})Cl_2$	23.2	5.3 (5.76)[d)]	115	255
$Cu(3,2,3\text{-tet})Cl_2$	21.7	5.0 (5.51)	150	230
$Cu(cyclam)Cl_2$	26.5	5.0 (5.11)	95	315[e)]

a) $\log K_1$ (Cu^{2+}).[7] b) I and II denote the first and second endothermic reactions in the DTA curve. c) Peak corresponds to the temperature at which the reaction comes to the most. All three complexes show a strong and sharp peak in the DTA curves. d) Numbers in parentheses represent the calculated value for the monohydrate. e) Accompanied by a small shoulder at about 325 °C.

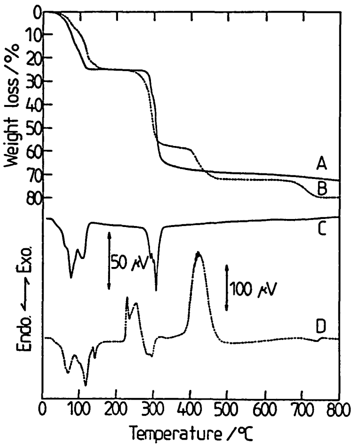

Fig. 2. TG and DTA curves of $Cu(3,2,3\text{-tet})SO_4$ under atmospheres of nitrogen and air.
——, in nitrogen; ----, in air. Sample weight: 50 mg. Heating rate: 5 °C min^{-1}.

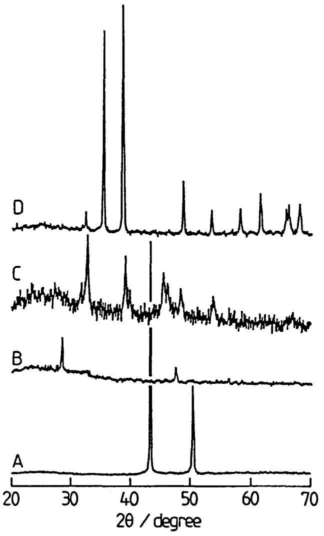

Fig. 3. X-ray diffraction diagrams for the residues after the thermal analyses of $Cu(3,2,3\text{-tet})Cl_2$ and $Cu(3,2,3\text{-tet})SO_4$ under atmospheres of nitrogen and air.
Temperature was raised up to 800 °C.
A, copper metal[5a)] from chloride, in nitrogen.
B, copper(I) chloride[5b)] from chloride, in air.
C, copper (I) sulphide (chalcocite, syn.[5c)]) from sulphate, in nitrogen.
D, copper(II) oxide[5d)] from sulphate, in air.

trary to our presumption. Therefore, a strong exothermic reaction over the temperature range from 420 to 700 °C includes such oxidation reactions as the combustion of carbonaceous products and the chlorination of copper metal to coppre(I) chloride. A small percentage of the residue arises from the volatility of copper(I) chloride dimer (Cu_2Cl_2)[8] (the percentage found, 7%; the one calculated for CuCl, 30.3%). The decomposition process of other complexes in air is the same as that of Cu(3,2,3-tet)Cl_2, and their thermal stabilities are consistent with their complex formation constants (Table 1).

Figure 2 shows the TG and DTA results of the sulfate, Cu(3,2,3-tet)SO_4, in air and in nitrogen. The thermal decomposition in a nitrogen atmosphere proceeds in a simple manner (Figs. 2A and C). Six moles of water per 1 mole of Cu(3,2,3-tet)SO_4 (weight loss found for $6H_2O$, 24.6; calcd 24.46%) were released up to about 120 °C. Compared with the results of the chloride (Figs. 1A and C), a major part of the ligand of the sulfate complex must begin to decompose above 270 °C. The ESR spectrum of a sample heated at 300 °C shows only one resonance line due to some of organic radical (g=2.00). The small Q-value observed for products above 300 °C most likely results from the existence of electro-conductive matter. As illustrated in Fig. 3, the product at 800 °C under an atmosphere of nitrogen is chalcocite[5c)] (copper(I) sulfide), which has a high electro-conductivity. Therefore, the sulfate complex decomposed directly to chalcocite and degraded amine moieties; the latter carbonized and graphitized upon further heating. Since the calculated content of copper(I) sulfide corresponded to 18.0% of the original sulfate complex, the residue at 800 °C contained carbon of about 9% in the TG curve. Taking into consideration that copper(II) sulfate pentahydrate forms copper(I) oxide at 800 °C upon heating under a nitrogen atmosphere, it is interesting that the copper(II) sulfate with polyamine is not transformed into copper(I) oxide. It is also interesting to produce copper(I) sulfide through thermal decompoition above 300 °C, since a pure form is generally prepared by the reaction of copper metal with hydrogen sulfide above 400 °C.[9] Both of the open-chain polyamine complexes in this study did not differ regarding thermal stability, since they start pyrolyzing at about 270 °C and complete the reaction to copper(I) sulfide below 330 °C. The sulfate complexes are more thermally stable than are the chloride types.

The results of a thermal analysis of Cu(3,2,3-tet)SO_4 in air are given in Figs. 2B and D. The exotherm at 230—270 °C appears to represent the degradation of a part of the 3,2,3-tet molecule, which is the same reaction as that at 240 °C in the DTA curve of the chloride (* in Fig. 1D). Two endotherms, one below 150 °C due to a dehydration reaction and the other at 270—310 °C due to the decomposition of the complex to form an undetermined copper species and carbonaceous products, resemble well those of the DTA curve up to about 320 °C in nitrogen. The strong exothermic peak centered around 420 °C is attributable to the combustion of the residual carbon, the remainder (at 500 °C) being a mixture of copper(II) oxide and its sulfate (Cu_2OSO_4). Decomposition to the oxide was observed by a weight decrease of about 7% in the final step of the TG curve due to the evolution of sulfur trioxide[10] accompanying a weak endotherm at about 740 °C. The ESR spectrum of the unidentified substance at about 310 °C (described above) revealed the formation of agglomerated copper in the divalent state,[11] as well as some organic radical (g=2.00); the intensity of the former signal was very small compared with that of the original complex. A further investigation is needed to determine whether the formation of a monovalent or an agglomerated divalent copper species results in a decrease in the intensity of the ESR signal.

The easy formation of copper(I) sulfide is consistent with the HSAB theory and the stability of the sulfide, even at elevated temperature.

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