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Intermediate phases and products of thermal decomposition of the compound $Tl_2Pb[Cu(NO_2)_6]$

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Abstract

The stoichiometry of the thermal decomposition of the compound $Tl_2Pb[Cu(NO_2)_6]$ has been studied. It is shown that the composition of the intermediate phases depends on the atmosphere in the reaction space, the composition of the intermediate phases being different when the decomposition is carried out in nitrogen or in air. As intermediate phases produced during decomposition under a nitrogen atmosphere, Cu_2O and $Pb(NO_3)_2$ were formed at 280°C. At the same temperature in an air atmosphere there were identified $TlNO_3$, $Pb_6O_5(NO_3)_2$ and $Tl_{5.1}PbO_{9.15}$ as intermediates. Further heating of this system led to the subsequent crystallization of Tl_2O_3, CuO and, probably, $Tl_6Pb_2O_5$ (520°C). As the final product of the decomposition a mixture of CuO, Tl_2O and PbO was identified.

INTRODUCTION

The possibility of preparing coordination compounds which contain several different metal atoms offers an opportunity to use them as starting materials for the synthesis of multiphase systems with homogeneously distributed phases. To these groups of complexes belong also the compounds $M^I_2M^{II}[Cu(NO_2)_6]$. These complexes are isostructural, possessing elpasolite (K_2NaAlF_6) type cubic (F_{mmm}) structure [1]. The positions of AlF_6^{3-} anions in the the structure of the the hexanitrocuprates are occupied by $[Cu(NO_2)_6]^{4-}$ anions, the positions of Na by the M^{II} atoms and the positions of K by M^I (Fig. 1). The crystals of hexanitrocuprates, however, are chiefly tetragonal or orthorhombic. This crystal symmetry lowering is connected with the tetragonal or rhombic shape of $[Cu(NO_2)_6]^{4-}$, caused by the Jahn–Teller instability of the Oh symmetry at Cu^{II} (d^9) compounds. The only compounds found to be cubic (with an octahedral

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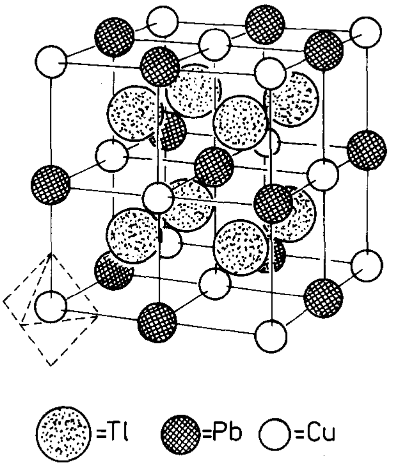

Fig. 1. Crystal structure of $Tl_2Pb[Cu(NO_2)_6]$.

complex anion) at room temperature were $K_2Pb[Cu(NO_2)_6$ [2] and $Tl_2Pb[Cu(NO_2)_6]$ [3]. However, the octahedral shape of $[Cu(NO_2)_6]^{4-}$ is a result of dynamic three-dimensional Jahn–Teller deformation of the anion in the directions of the principal axes of the octahedron. When cooled, both compounds undergo phase transitions to orthorhombic symmetry [4, 5]. This symmetry reduction is connected with the change of the complex anion site symmetry from octahedra to tetragonal or rhombic. Compounds with $M^I = Rb$ or Cs and $M^{II} = Pb$ undergo orthorhombic to cubic phase transitions when heated to 40°C (Rb) or 120°C (Cs) [6], and these transitions are again caused by symmetry changes of the $[Cu(NO_2)_6]^{4-}$. No phase transitions of this type were observed for compounds with $M^{II} = Ca$, Sr and Ba [7]; however, there were some indications of a two-dimensional dynamic Jahn–Teller effect in the equatorial plane of the $[Cu(NO_2)_6]^{4-}$ anions.

The thermal decomposition of the complexes $M^I_2M^{II}[Cu(NO_2)_6]$, where M^I was K, Rb or Cs and M^{II} was Ca, Sr, Ba or Pb has been studied [8], and although the decomposition temperatures were found to be dependent on the outer sphere cation present, the decomposition stoichiometry was concluded to be identical for all the studied compounds

$$2M^I_2M^{II}[Cu(NO_2)_6] \rightarrow 4M^INO_3 + M^{II}O + M^{II}(NO_3)_2 + 2CuO + 6NO_x$$

The M^I and M^{II} nitrates decompose at higher temperatures to the respective oxides. Until now, the thermal decomposition of compounds containing thallium as counter cation had not been studied. Among the compounds $Tl_2M^{II}[Cu(NO_2)_6]$, only the crystal structure of the compound with $M^{II} = Pb$ was known up to now [3]. Although the course of the decomposition of all thallium containing compounds is of interest, we started with this one. Accordingly, we have prepared complexes

$Tl_2M^{II}[Cu(NO_2)_6]$ with M^{II} = Ca, Sr or Ba, identified their crystal structures and studied their thermal decomposition. The results are to be published in a subsequent paper.

EXPERIMENTAL

Synthesis and analytical methods

The compound $Tl_2Pb[Cu(NO_2)_6]$ was prepared according to [9]. For determination of the composition of the compound the usual chelatometric methods were used. $Tl_2Pb[Cu(NO_2)_6]$, MW 859.53 g mol^{-1}, Pb calc. 21.68%, found 21.72%, Cu calc 6.65%, found 6.66%. The powder pattern of the compound was taken, and indexation of the diffractions according to the crystal structure data on this compound showed that a pure compound had been prepared.

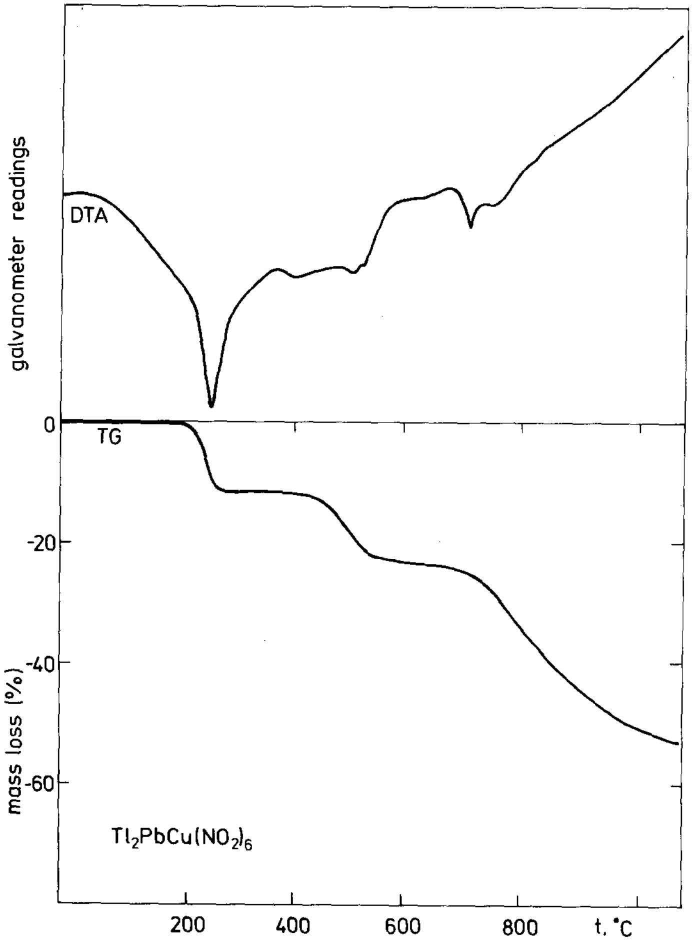

Fig. 2. The course of thermal decomposition of $Tl_2Pb[Cu(NO_2)_6]$.

Thermal decomposition of the compound was carried out with an OD 102 derivatograph (MOM Budapest, Hungary). The sample mass was 100 mg, and the heating rate was 10°C min^{-1} over the range 20–1000°C. Measurements were made in an air atmosphere. The intermediates of the decomposition were prepared by isothermal heating of $Tl_2Pb[Cu(NO_2)_6]$ to temperatures corresponding to the plateaux observed on the TG curve (Fig. 2). The X-ray diffraction patterns of the intermediates were obtained using a GON-2 powder goniometer (Czech production); Cu Kα radiation and a Ni filter were used. The resulting powder patterns were evaluated using the JCPDS data base. The intermediate of the first decomposition reaction was also prepared in a capillary in a nitrogen atmosphere, using a STOE Bragg–Brentano diffractometer. Using the same experimental arrangement, we followed the changes in the structure and composition of the compound during heating to the decomposition temperature.

RESULTS AND DISCUSSION

Thermal decomposition of the complex $Tl_2Pb[Cu(NO_2)_6]$ starts at a temperature of 220°C (Fig. 2). However, some changes are obvious from the DTA curve below this temperature. The low-temperature shoulder on the DTA curve corresponds to an endothermic reaction, which precedes the escape of volatile products. This reaction was studied qualitatively on a heated stage microscope, and it was found that in the range 160–180°C a

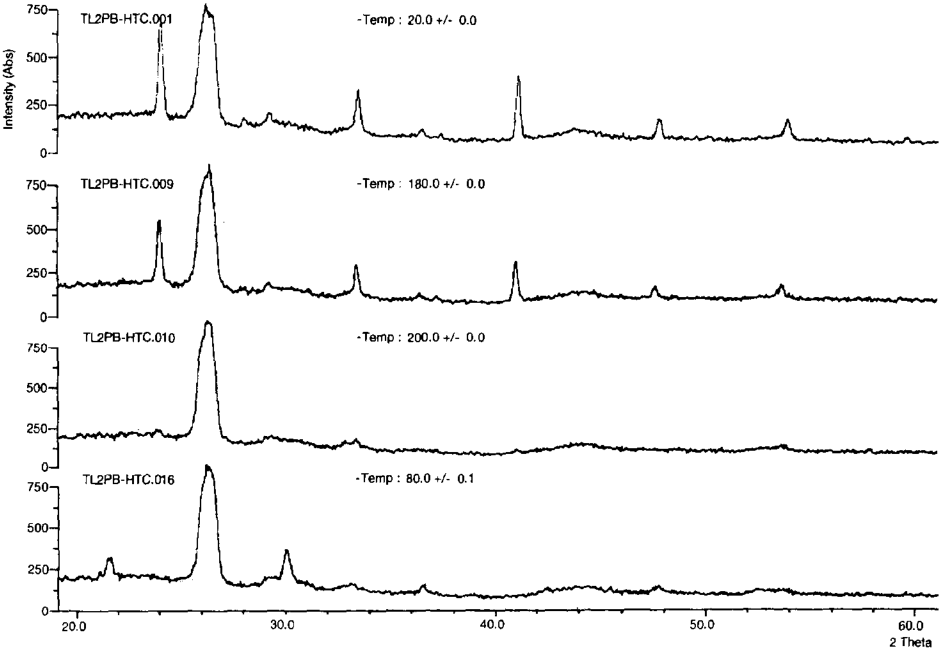

Fig. 3. Changes in the X-ray powder pattern of $Tl_2Pb[Cu(NO_2)_6]$ during heating.

white substance sublimes from the compound. Powder patterns taken in this temperature range in a capillary under nitrogen showed (Fig. 3) that the crystal structure of the compound broke down, the sample at this temperature being X-ray amorphous. After cooling, a new phase or a combination of new phases was observed.

The intermediate was still amorphous at 280°C, at which temperature, according to the TG curve, the first decomposition reaction was complete. In the decomposition intermediate, Cu_2O and $Pb(NO_3)_2$ were identified, and some diffraction lines remained which could not be assigned (see Fig. 4). No thallium compounds were identified in the reaction mixture therefore we have also to assume the presence of a non-diffracting phase. The composition of the crystalline products indicates clearly an inner-complex reaction taking place in the first step of thermal decomposition of the compound. The reduction of Cu^{II} to Cu^{I} is accompanied by oxidation of NO_2^- to NO_3^-.

When the decomposition of the compound is carried out in an air atmosphere, the intermediate produced at 280°C contains, according to its powder pattern (Fig. 5), $TlNO_3$, $Tl_{5.10}PbO_{9.15}$ [10] and, probably,

TABLE 1

X-ray powder patterns of the intermediates of the thermal decomposition of $Tl_2Pb[Cu(NO_2)_6]$ at 520°C (A) and 900°C (B)

A			B		
d(Å)	I_r	Compounds identified	*d* (Å)	I_r	Compounds identified
4.31	10	Tl_2O_3			
3.05	100	Tl_2O_3, PbO, $Tl_6Pb_2O_5$	3.12	83	Tl_2O
			3.07		
2.94	26	PbO	2.94	100	PbO
			2.87	17	Tl_2O
			2.81	28	Tl_2O
			2.75	19	Cu
2.74	10	PbO, CuO	2.74	19	PbO
2.67	10	$Tl_6Pb_2O_5$			
2.64	42	Tl_2O_3, $Tl_6Pb_2O_5$			
			2.53	60	CUO
2.49	10	Tl_2O_3, $Tl_6Pb_2O_5$			
			2.38	18	PbO
			2.33	43	CuO
2.07	11	Tl_2O_3			
			2.01	12	PbO
1.87	44	CuO, Tl_2O_3, $Tl_6Pb_2O_5$			
1.72	10	CuO, PbO	1.72	30	CuO, PbO
1.59	36	Tl_2O_3, CuO, $Tl_6Pb_2O_5$	1.58	10	CuO

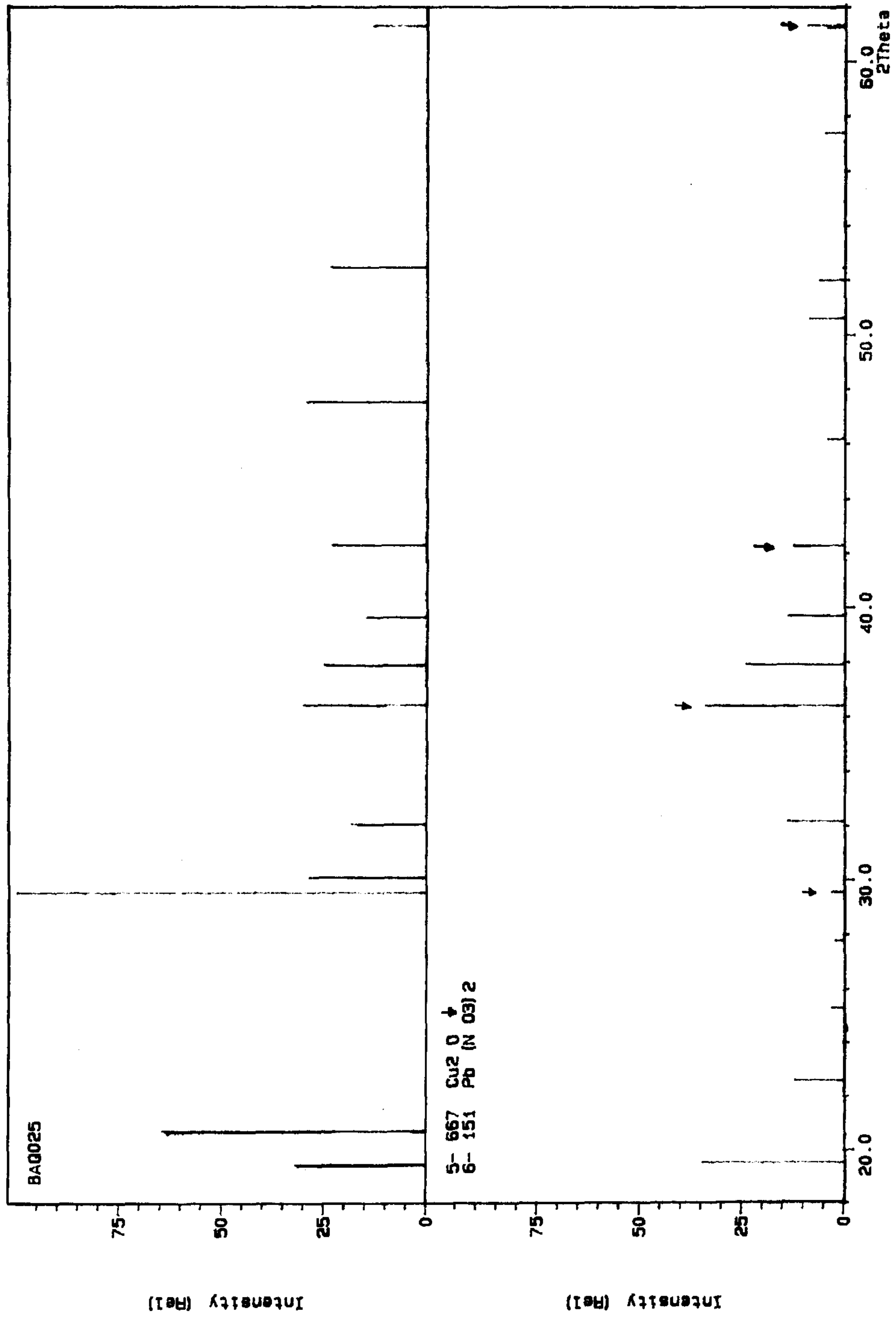

Fig. 4. X-ray powder pattern of intermediate of decomposition of $Tl_2Pb[Cu(NO_2)_6]$ at 280°C in nitrogen.

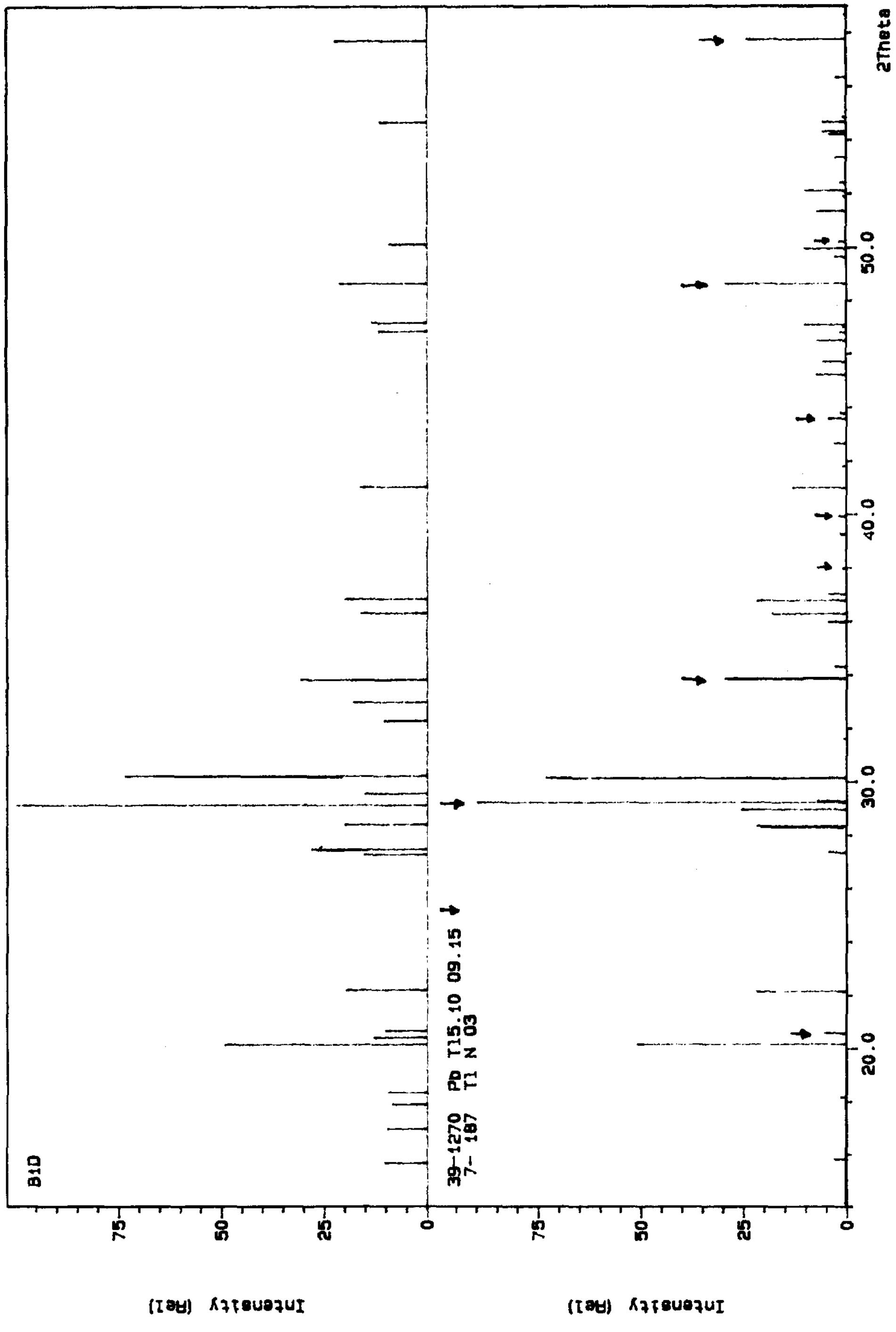

Fig. 5. X-ray powder pattern of intermediate of decomposition of $Tl_2Pb[Cu(NO_2)_6]$ at 280°C in air.

$Pb_6O_5(NO_3)_2$ [11]. The crystal structures of the last two compounds are not known. The compound $Pb_6O_5(NO_3)_2$ appears as an intermediate of the thermal decomposition of $Pb(NO_3)_2$ and is stable up to 390°C; its decomposition product is PbO_x [11]. On the basis of the X-ray powder pattern, no copper compound was identified in this decomposition intermediate. After further heating of this mixture to 520°C, Tl_2O_3, CuO and $Tl_6Pb_2O_5$ were identified in the mixture (Table 1). In the X-ray pattern, however, the most intense diffraction lines ($d = 3.04$, 2.65 and 2.48 Å) of both thallium compounds are nearly identical according to the ASTM data base. It is therefore impossible to decide whether both thallium containing compounds are really present in the mixture. Only simple oxides of Cu^{II}, Tl^{I} and Pb^{II} were identified (Table 1) in the reaction mixture after heating to 900°C.

In conclusion, we can state that the reaction product is a multiphase system. The structures of individual phases when compared with the ASTM data were not ideal in respect of the *d*-values. This may be a consequence of solid solution formation, impurity content or another type of structural disorder.

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