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THERMAL DECOMPOSITION OF COPPER COMPLEXES OF 1-PHENYL-3-METHYL-4-ACYL-5-PYRAZOLONE IN AIR ATMOSPHERE

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Abstract

Copper complexes of some 1-phenyl-3-methyl-4-acyl-5-pyrazolones have been prepared. The complexes were characterized by elemental analyses and thermal analyses. It was shown that the melting points decrease linearly in increasing the molecular weight of the complexes.

Keywords: complexes, copper complexes of 1-phenyl-3-methyl-4-acyl-5-pyrazolone

Introduction

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolones (PMBP) and its 4-acyl derivatives are suitable agents for the extraction of metals, because of their high reactivity and the stability of their complexes. Numerous studies have been made on metal extraction and separation with these agents [1–3]. Spectroscopic studies have also been carried out on the Mn and Zn complexes of 4-acyl-pyrazolone [4]. We recently reported the synthesis and thermal properties of PMBP complexes of various trivalent metals. For the Al, Ga and In complexes of PMBP, a linear relationship was observed between the melting points of the complexes and the ionic radii of the central metal ions.

Thermogravimetry (TG) and differential thermal analysis (DTA) are valuable techniques for study of the thermal properties of various compounds. However, no systematic study has been made of the thermal behavior for the metal complexes of PMBP or its 4-acyl derivatives. This work is a continuation of studies [5–7] on the thermal decompositions of chelate compounds formed between various heavy metals and PMBP or its 4-acyl derivatives. In the present work, we describe the preparation and thermal properties of copper complexes with systematically synthesized ligands: 1-phenyl-3-methyl-4-acyl-5-pyrazolone derivatives of the type $(C_{10}H_9N_2O)(C_nH_{2n+1})$ (n=2–10).

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Experimental

The ligands 1-phenyl-3-methyl-4-acyl-5-pyrazolones (C_N) were prepared by a method analogous to that for PMBP preparation [8]. Here, the reagents are represented by C_N, where N means the number of carbon atoms in the acyl chain (C_nH_{2n+1} CO, $N=n+1$). The copper complexes of the pyrazolone and an aqueous solution of copper sulfate in a 2:1 molar ratio. The resulting solid was collected by filtration and was washed several times with methanol by stirring and dried in a vacuum oven. The composition of these chelates was found by elemental analysis in each case to be Cu:C_N=1:2. The analytical data are listed in Table 1. Thermal analysis studies were carried out with a Rigaku Denki Model 8100 operating at a chart speed of 2.5 cm·min^{-1}. Samples of about 6 mg were heated in an open aluminum crucible in air atmosphere at a heating rate of 10 deg·min^{-1}, up to 600°C. The reference compound used was ground alumina.

Table 1 Elemental analyses of Cu complexes

	C/%		H/%		N/%	
	Found	Calc.	Found	Calc.	Found	Calc.
Cu-C_3	60.2	59.8	4.8	5.0	10.9	10.7
Cu-C_4	60.5	61.1	5.5	5.5	10.4	10.2
Cu-C_5	61.4	62.3	5.8	5.9	9.6	9.7
Cu-C_6	62.1	63.4	6.2	6.3	8.9	9.2
Cu-C_7	63.1	64.4	6.6	6.7	8.7	8.8
Cu-C_8	64.5	65.3	6.9	7.0	8.0	8.5
Cu-C_9	66.5	66.1	7.4	7.3	8.4	8.1
Cu-C_{10}	66.0	66.9	7.5	7.6	7.4	7.8
Cu-C_{11}	66.0	67.6	8.0	7.8	7.4	7.5

Results and discussion

Thermal analysis was carried out systematically for the copper 4-acyl-pyrazolonates in air atmosphere. Figure 1 illustrates the TG and DTA curves of the complex Cu–C_4 heated from room temperature to 600°C. It can be seen that the compound melts endothermally at 249°C, followed by degradation at about 273°C (first step), with beginning of decomposition of the ligands. The melting point was not observed when the complex Cu–C_3 was heated in air atmosphere, indicating that melting and decomposition of the compound may occur simultaneously at 287°C. However, the endothermic melting of the complex Cu–C_3 was clearly observed at 289°C when it was heated in N_2 atmosphere, as shown in Fig. 2. TG and DTA curves of Cu–C_8 and Cu–C_{11} are shown in Figs 3 and 4,

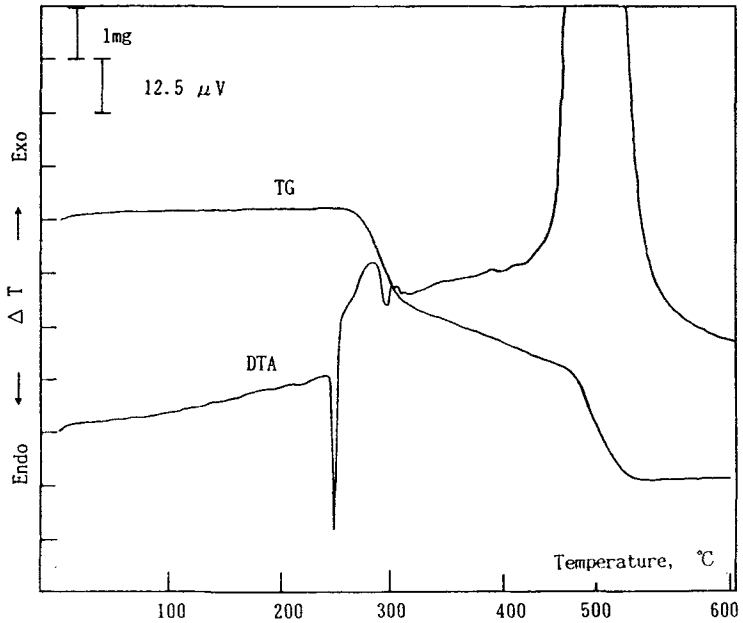

Fig. 1 TG and DTA curves of Cu–C_4 complex. Sample mass: 6.0 mg, heating rate: 10 deg·min^{-1}, atmosphere: air

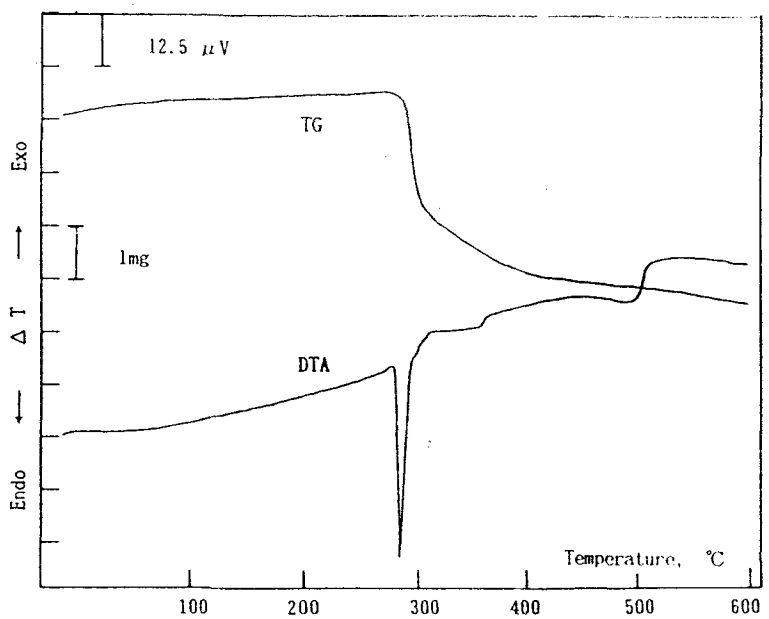

Fig. 2 TG and DTA curves of Cu–C_3 complex. Sample mass: 5.7 mg, heating rate: 10 deg·min^{-1}, atmosphere: N_2

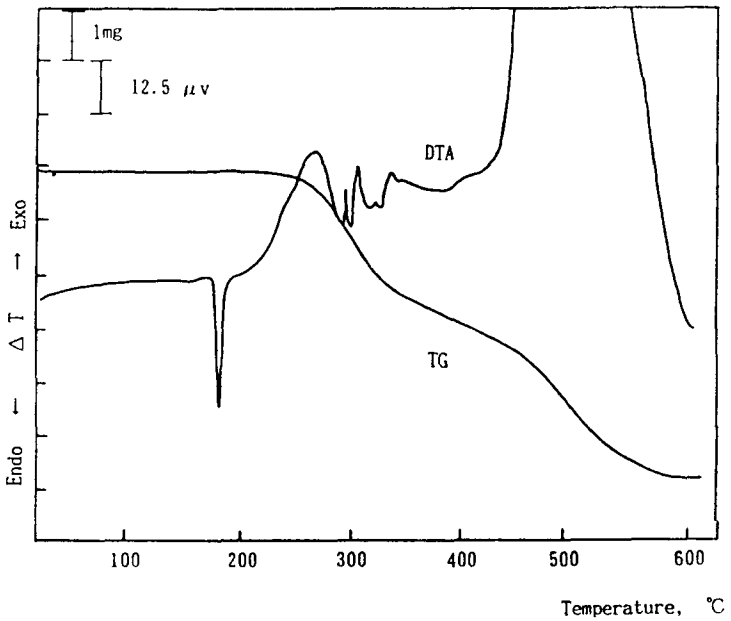

Fig. 3 TG and DTA curves of Cu–C_8 complex. Sample mass: 8.2 mg, heating rate: 10 deg·min^{-1}, atmosphere: air

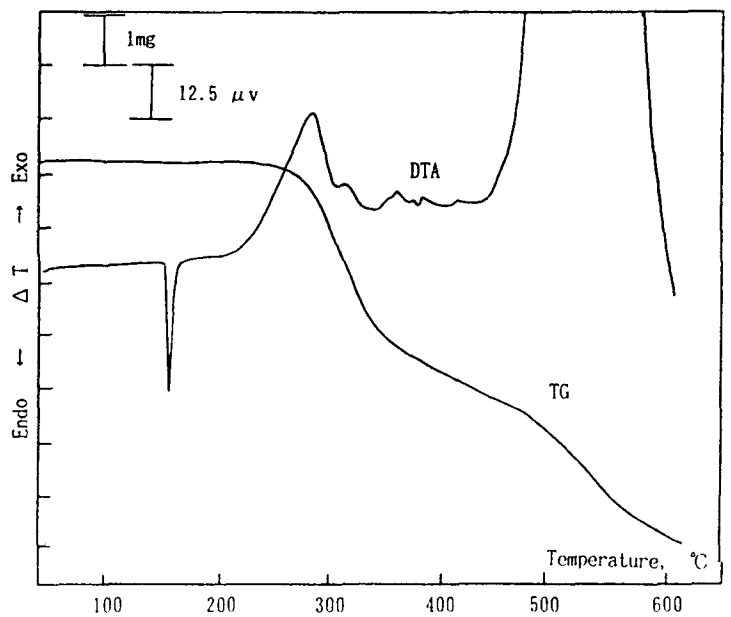

Fig. 4 TG and DTA curves of Cu–C_{11} complex. Sample mass: 7.6 mg, heating rate: 10 deg·min^{-1}, atmosphere: air

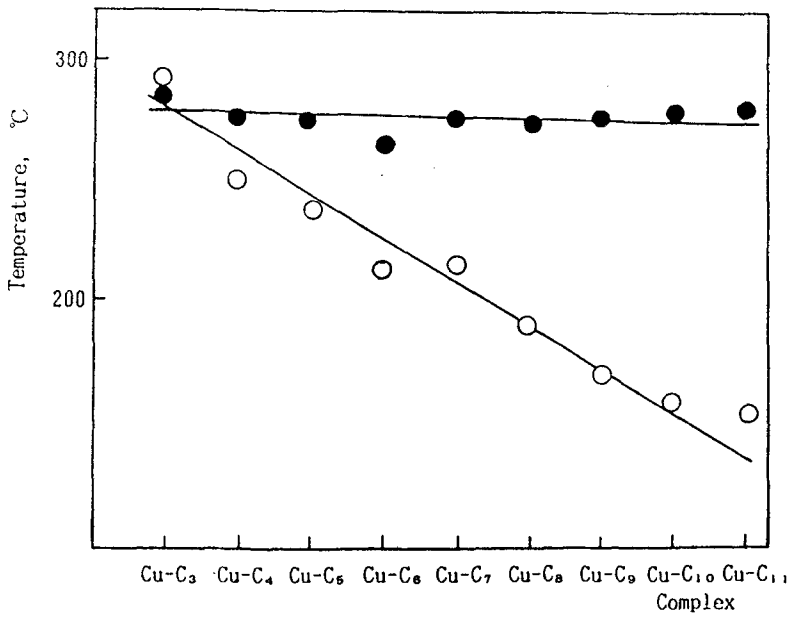

Fig. 5 Plots of melting point (o) and beginning of decomposition temperature (•) for the complex. All measurements were done in air atmosphere except for the Cu–C_3 complex, its melting point was measured in the N_2 atmosphere

respectively. The complexes Cu–C_3~Cu–C_{11} all decompose in two steps in the temperature range above 270°C.

The decomposition products in this range are mixtures of copper oxide and carbon. For the complex Cu–C_4, the final loss in mass occurs at 473°C; thereafter, the TG curve shows a stable horizontal plateau up to 600°C, where a residue of ca. 18% of the sample mass is obtained. The final product of decomposition of the complex in air atmosphere is CuO.

The melting temperatures of the complexes Cu–C_N depend on the molecular weights of the ligands. The melting points presented in Fig. 3 reveal a linear decrease with increasing molecular weight of the complexes. This tendency was not observed for the ligands, whose melting temperatures were in the range 65–67°C. On the other hand, the initial temperatures of decomposition of the complexes and the temperatures of formation of copper oxide do not depend on the molecular weights of the ligands. From a comparison with the temperatures of decomposition of the copper pyrazolonate series, it is possible to suggest that the thermal stability is approximately the same for all these compounds.

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Zusammenfassung — Es wurden die Kupferkomplexe einiger 1-Phenyl-3-methyl-4-acyl-5-pyrazolone (PMBP) hergestellt und mittels Elementaranalyse und Thermoanalyse charakterisiert. Es wurde gezeigt, daß die Schmelzpunkte mit steigendem Molekulargewicht der Komplexe linear abnehmen.