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THERMAL DECOMPOSITIONS OF COMPLEXES OF Al, Ga, In, Cr, Fe AND Bi IONS WITH 1-PHENYL-3-METHYL-4-BENZOYL-5-PYRAZOLONE

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Abstract

The thermal decompositions of Al, Ga, In, Cr, Fe and Bi complexes with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone have been studied in a nitrogen atmosphere. The thermal stabilities of these complexes follow the sequence Bi < Fe < Ga < In < Cr < Al. In the cases of Al, Ga and In, a linear relationship was obtained between the melting points of the complexes and the ionic radii of the central metals.

Keywords: complexes, thermal decomposition, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone

Introduction

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) forms stable complexes with various metal ions at relatively low *pH*. Numerous studies [1–4] have been made concerning the separation of trace metal ions by using this chelating agent. However, the thermal properties of metal–PMBP complexes are little known [5]. Previously, the complex Fe(III)–PMBP was prepared and characterized by thermal analysis [6]. We have now extended this thermochemical study of metal–PMBP complexes to other elements. This paper describes the synthesis of the PMBP complexes of Al, Ga, In, Cr and Bi and their thermal characterization during heating in a nitrogen atmosphere.

Experimental

Each metal pyrazolonate was prepared by mixing the appropriate metal salt and a methanolic solution of PMBP in a molar ratio of 1:3 at approximately *pH* 3. The mixture was allowed to react thoroughly in a water-bath at 70–80°C. The precipitate was washed with deionized water after filtration. The product

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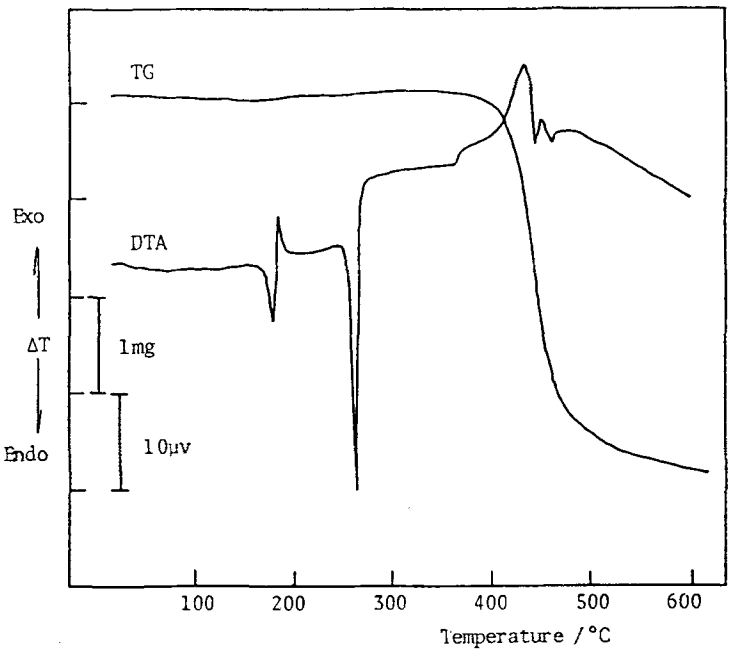

Fig. 1a TG and DTA curves of $Al(PMBP)_3$

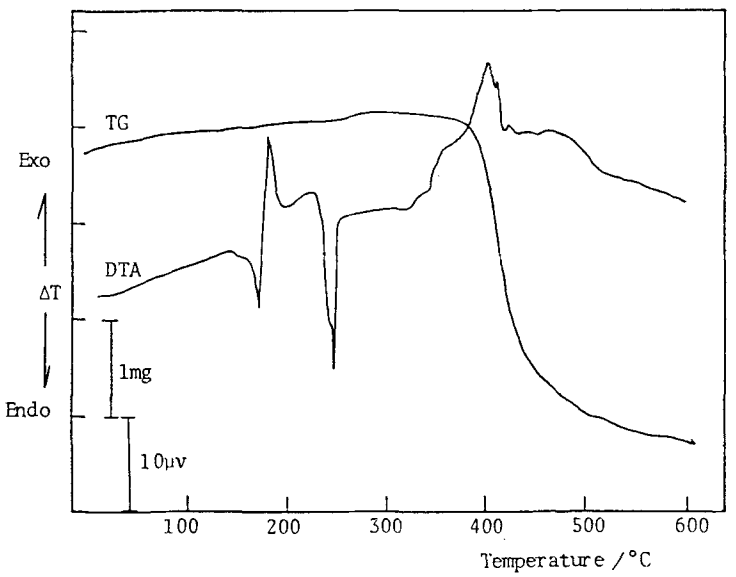

Fig. 1b TG and DTA curves of $Ga(PMBP)_3$

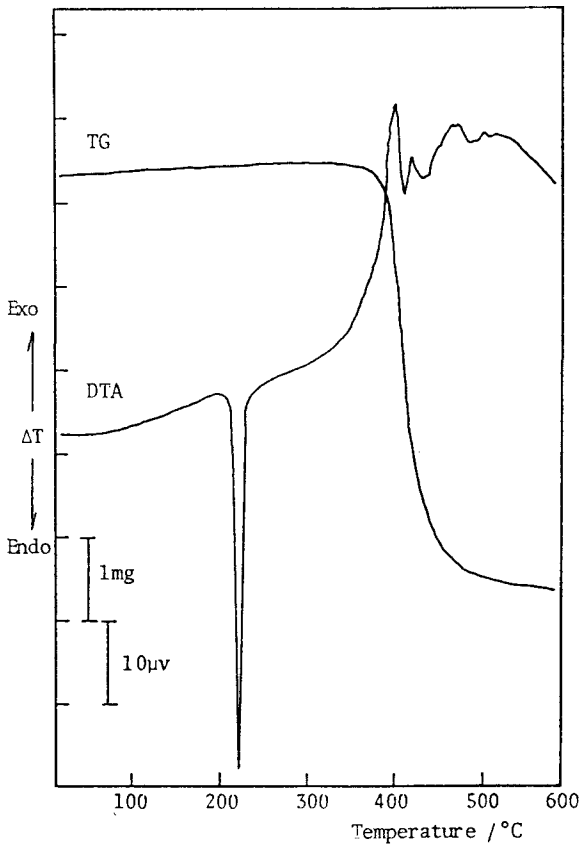

Fig. 1c TG and DTA curves of $In(PMBP)_3$

was then stirred with a little methanol during heating, to remove the unreacted PMBP. After separation of the two phases, the purifying process was repeated twice. Each precipitate was then dried under vacuum and characterized by elemental analysis as $M(PMBP)_3$. Thermal analysis studies were carried out using a Rigaku Denki Model 8100 series working at a chart speed of 2.5 mm/min. Samples of ca 5 mg were heated in an open aluminum crucible in nitrogen atmosphere at a heating rate of 10 deg·min^{-1}, up to 600°C. The reference compound used was ground alumina.

Results and discussion

TG and DTA curves of the Al, Ga and In complexes of PMBP are presented in Fig. 1. These complexes were thermally stable up to 350–360°C, and then decomposed with mass loss to mixtures of carbon and metal oxides. The endo-

thermic peak at 181°C and the just subsequent exothermic peak are shown for the Al complex; no mass change was observed at this temperature in the TG curve. The complex melted at 263°C. As the temperature was raised further, the DTA curve exhibited a large exothermic peak at 433°C. This peak was accompanied by a 58% loss in mass, possibly due to the decomposition of the three PMBP ligand molecules.

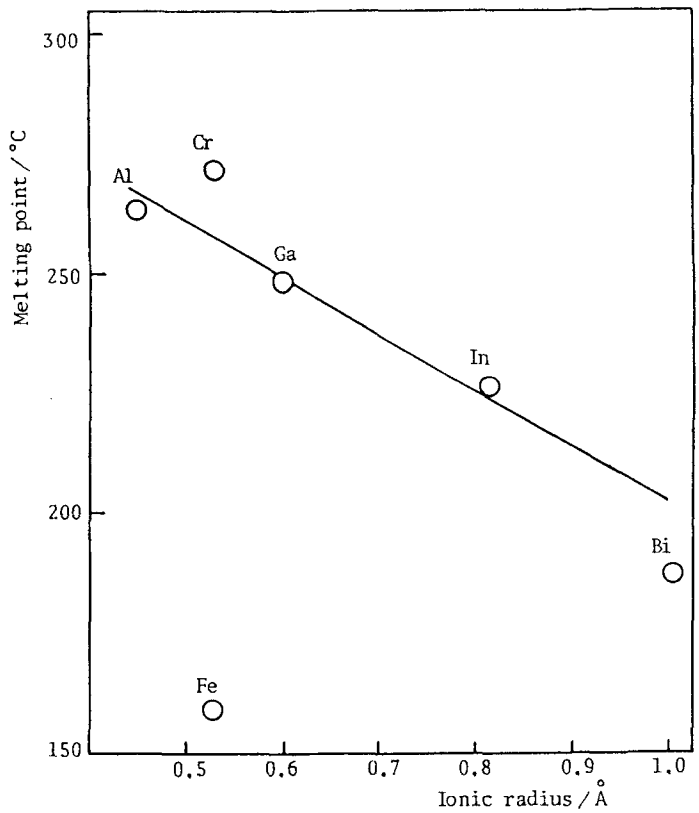

Fig. 2 Plots of melting point of the complex *vs.* ionic radii of the central metal

The results demonstrate that the thermal behaviour of the Al complex at 181°C in the DTA curve reveals a solid–solid transformation of the complex. The DTA curves for the Ga and Cr complexes were similar to those for the Al complex, whereas the endothermic and exothermic peaks before the melting point were not observed for the In and other complexes. Strong endothermic peaks were observed for the Ga, In, Cr, Fe and Bi complexes of PMBP at 249, 227, 272, 159 and 187°C, respectively, due to their phase change on melting, i.e. the corresponding temperature increased in the sequence

$$Fe < Bi < In < Ga < Al < Cr.$$

In the cases of Al, Ga and In, a good linear relationship was obtained between their melting points and the ionic radii of the central metals, as shown in Fig. 2. However, the melting point of the Fe complex was well below this line. This sequence may indicate that a smaller ionic radius makes a great contribution to the stabilization of the complex produced on coordination between the metal and the ligand. The onset of the loss in mass observed at about 364, 353 and 355°C for the Al, Ga and In complexes corresponded to decomposition of the PMBP ligand. For the In complex, about 20% of the mass was eliminated due to the decomposition of three molecules of PMBP and the formation of metal oxide and carbon. The TG curve was nearly the same for all the complexes involved in this study, indicating that each complex decomposed in one step at or before 600°C.

Plots of the melting points *vs.* the temperatures of the initial decompositions of these complexes were also approximately linear, as shown in Fig. 3; the data for the Bi complex did not lie on the line.

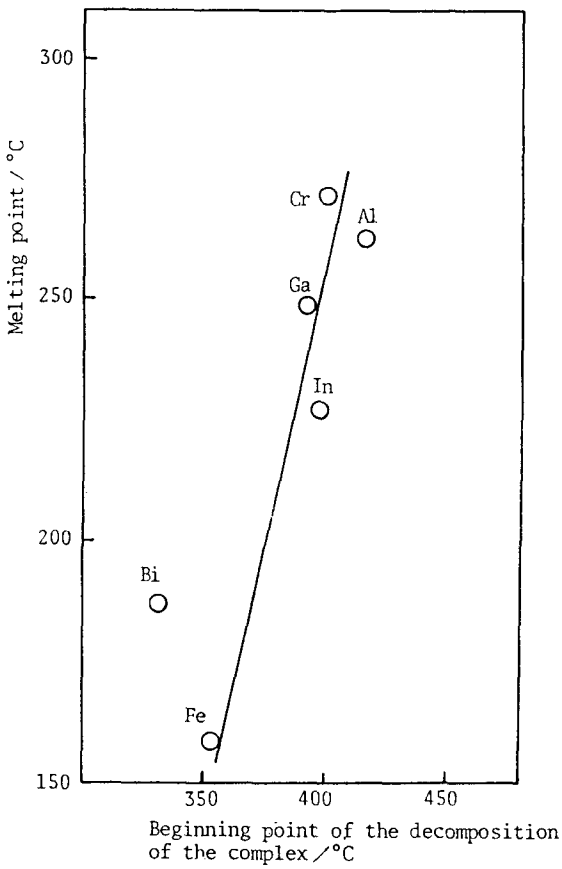

Fig. 3 Plots of melting point *vs.* decomposing point for the complex

To summarize, the pyrazolonate complexes of trivalent metals (M) have the stoichiometry $M(PMBP)_3$. Thermal analyses of the Al, Ga, In, Cr, Fe and Bi complexes of PMBP show that they undergo exothermic reactions at temperatures in the range 332–416°C, in each case the PMBP decomposing. The nature of the plot in Fig. 2 suggests a linear relationship between the melting points and the ionic radii in certain cases. The difference in the melting temperatures for the Al and In complexes was about 36 deg. It is suggested that the stable structure of the complex involved coordination between the smaller central metal ion and the ligands.

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Zusammenfassung — In Stickstoffatmosphäre wurde die thermische Zersetzung von Al-, Ga-, In-, Cr-, Fe- und Bi-Komplexen mit 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolon untersucht. Die thermische Stabilität dieser Komplexe steigt in der Reihenfolge Bi < Fe < Ga < In < Cr < Al. Im Falle von Al, Ga und In erhielt man einen linearen Zusammenhang zwischen Schmelzpunkt der Komplexe und dem Ionenradius der zentralen Metalle.