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THERMAL DECOMPOSITION OF IRON(III) COMPLEX OF 1-PHENYL-3-METHYL-4-BENZOYL-5-PYRAZOLONE

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Abstract

A pyrazolonate (PMBP) of iron(III) was prepared and its metal to ligand stoichiometry was shown to be 1:3. The decomposition of the complex was studied by thermogravimetry and differential analyses under an air atmosphere. The complex undergos two endothermic reactions without loss in mass, at 160 and 218°C, followed by an exothermic reaction at 480°C involving decomposition of the ligands. Intermediates obtained by melting of the Fe–PMBP complex were characterized by X-ray diffraction analysis. The Fe–PMBP complex was confirmed by HPLC to be a mixture of two isomers.

Keywords: complexes, iron(III) complex of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, thermal analysis

Introduction

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) has been extensively employed for the efficient extraction separation of many cations. In previous papers, we have described atomic absorption spectrometry [1, 2] and high-performance liquid chromatography [3–5] for many cations, with PMBP as chelating agent. PMBP reacts with Fe(III) and V(V) to form water-insoluble reddish crystalline complexes. These reactions have been used for the spectrophotometric determination of Fe(III) [6] and V(V) [7]. Furthermore, thermal decomposition studies have been made on ternary adducts of uranyl pyrazolonate [8]. However, a search of the available literature revealed that no attention has been paid to the thermal decompositions of other metal pyrazolonates. Therefore, it was thought worthwhile to investigate such complexes from a thermal stand-point. The present article, which forms part of systematic studies on

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the properties of metal–PMBP complexes, describes the thermal decomposition of Fe(PMBP)$_3$.

Experimental

The complex Fe(PMBP)$_3$ was synthesized by mixing iron alum and a methanolic solution of PMBP in a molar ratio of 1:3 at approximately *pH* 3. The reaction mixture was magnetically stirred in a beaker for 1 h in a water-bath at 70–80°C. The complex formed was filtered off, washed with distilled water and then recrystallized from a methanol+acetone (10+3) solution. The contents of carbon, hydrogen and nitrogen in the prepared complex were determined by elemental analysis. The content of iron was determined with a Hitachi 170–30 atomic absorption spectrometer. The analytical data are listed in Table 1. The results obtained correspond to the theoretical formula Fe(PMBP)$_3$. Thermal analysis studies were carried out with a Rigaku Denki Model 8100 operating at a chart speed of 2.5 cm/min.

Table 1 Elemental analysis of Fe–PMBP complex

Element	Calculated %	Found %
C	68.99	68.22
H	4.43	4.40
N	9.47	9.48
Fe	6.29	6.30

Fe(PMBP)$_3$ =887.753

Samples of ca. 8 mg were heated in an open aluminium crucible in air atmosphere at a rate of 10 deg·min^{-1}, up to 600°C. The reference compound was ground alumina. To confirm the composition of the intermediate compound, its IR spectrum was measured over the range 4000– 400 cm^{-1} with an FT-IR 5-MP DR-81 spectrometer (JASCO, Tokyo) using an ATR method. X-ray diffractograms were recorded with a Rigaku RINT-2500V diffractometer with CuK$_\alpha$ radiation, 50 kV/300 mA, a scanning speed of 2.0°/min and a scanning step of 0.02, without a filter.

Results and discussion

The simultaneous TG and DTA curves of the complex Fe(PMBP)$_3$ are given in Fig. 1. The thermal decomposition studies showed that Fe(PMBP)$_3$ is stable up to ca. 300°C and then decomposes in two steps. Fe(PMBP)$_3$ undergos two endothermic reactions, at 160 and 218°C, followed by an exothermic reaction at

480°C with decomposition of the ligands, burning of the organic ligand being accompanied by a strong exothermic effect. Thereafter, the TG curve displays a stable horizontal plateau up to the end of the heating program, where a residue

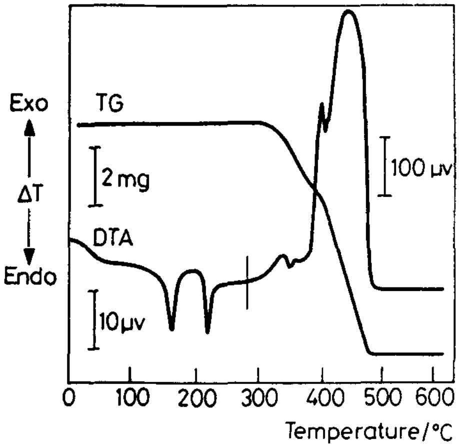

Fig. 1 TG and DTA curves of Fe(PMBP)$_3$ complex. The DTA full scale range was exchanged from 100 μV to 1000 μV at 280°C. Sample mass: 8.70 mg; Heating rate: 10 deg·min^{-1}; Atmosphere: air

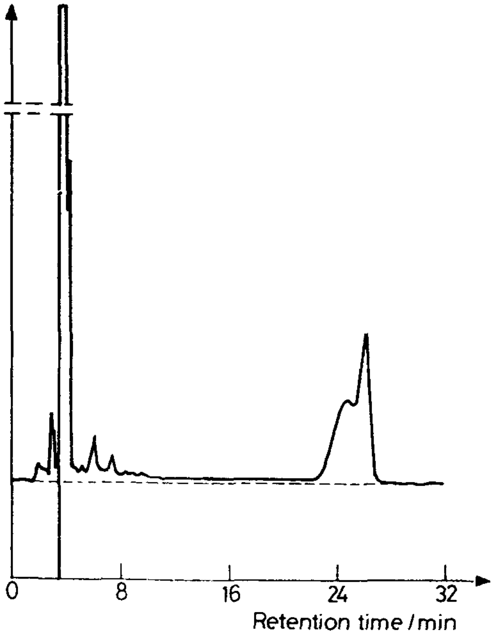

Fig. 2 Chromatogram for the Fe(PMBP)$_3$ complex. Concentration of Fe(PMBP)$_3$ complex in dioxane: 1.7·10^{-5} mol/l

of ca. 10% of the sample mass was obtained. The loss in mass (ca. 90%) in the TG profile of $Fe(PMBP)_3$ is attributed to decomposition of the PMBP ligands. The final product of decomposition of the complex in an air atmosphere is an oxide of iron (Fe_2O_3). To clarify the two endotherms at 160 and 218°C, the complex was heated up to 190 or 245°C, then cooled down to room temperature and subjected to thermal analysis, IR spectrum and X-ray diffraction measurements.

Further, the chromatographic behaviour of the complex, dissolved in dioxane, on an ODS column (Chemcosorb, 5-ODS-UH, 250×4.6 mm i.d.) was investigated by using a CH_3CN+H_2O (100+5) mixture as mobile phase at a flow rate of 1.0 ml/min, with UV detection at 245 nm. Two peaks corresponding to $Fe(PMBP)_3$, which were incompletely separated, were observed at around 26 min (Fig. 2), indicating the existence of two components, regardless of the high purity. The complex probably consists of two geometrical isomers. For the compound obtained from the parent compound by heating to 245°C and then cooling to room temperature in the sample chamber, the endotherm shown in Fig. 1 was not observed in the DTA curve.

A broader endothermic DTA curve was recorded (Fig. 3) in the temperature range 32–300°C. However, the pattern of the TG curve is similar to that obtained for the parent compound. Differences did not appear on comparison of the IR absorption spectra of the starting complex and the complex heated up to 190 or 245°C.

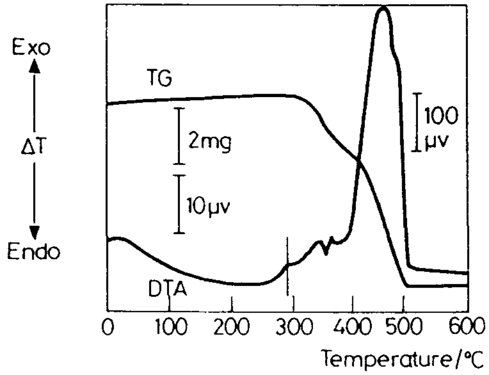

Fig. 3 TG and DTA curves of $Fe(PMBP)_3$ complex. The DTA full scale range was exchanged from 100 µV to 1000 µV at 295°C. After the $Fe(PMBP)_3$ complex was preheated up to 245°C and cooled to room temperature in the sample chamber, the thermal analysis was carried out again. Sample mass: 7.46 mg. Heating rate: 10 deg·min^{-1}; Atmosphere: air

The X-ray diffraction spectra of compound A (original complex), compound B (the original complex was heated up to 190°C and then cooled to room

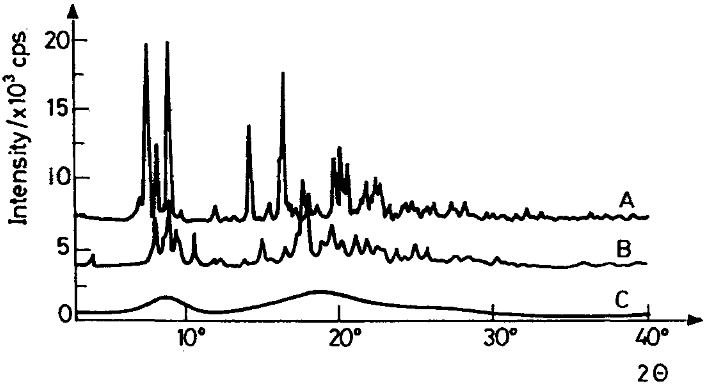

Fig. 4 X-ray diffraction sepctra of Fe(PMBP)$_3$ complex. A: Original complex, B: Original complex was heated up to 190°C then cooled to room temperature, C: Original complex was heated up to 245°C and then cooled to room temperature

temp.) and compound C (the original complex was heated up to 245°C and then cooled to room temp.) are shown in Fig. 4. The spectrum of the intermediate B is obviously different from that of A, and a slight decrease in crystallinity was observed. Finally, the X-ray diffraction profile of C revealed a broader peak, indicating the conversion of the original complex to an amorphous structure.

In conclusion, the two endotherms are due to the melting reaction of the complex, which probably exists as a mixture of geometrical isomers such as facial and meridional complexes. Further work concerning the thermal behaviour of complexes similar to Fe(PMBP)$_3$ is in progress.

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Zusammenfassung — Das Pyrazolonat (PMBP) von Eisen(III) wurde hergestellt und ein Metall–Liganden–Verhältnis von 1:3 ermittelt. Mittels TG und Differentialanalyse in Luft wurde die Zersetzung des Komplexes untersucht. Der Komplex unterliegt bei 160 und 218°C zwei endothermen Reaktionen ohne Masseverlust, gefolgt von einer exothermen Reaktion bei 480°C unter Zersetzung der Liganden. Zwischenprodukte des Fe–PMBP-Komplexes während des Schmelzvorganges wurden mittels Röntgendiffraktion charakterisiert. Mittels HPLC wurde der Fe–PMBP-Komplex als eine Mischung aus zwei Isomeren erkannt.