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THERMAL DEGRADATION OF METAL ACETYLACETONATES WITH DIVALENT METALS BY A COMBINED TG–DTA–MS TECHNIQUE

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ABSTRACT

This work deals with the application of a combined TG–DTA–MS apparatus with regard to its use in investigations of the thermal behaviour of metal complexes. Our interest was aimed at chelates of divalent transition metals (Me) of general formula Me(acac)$_2$ (acac = acetylacetone). It has been noted previously that the equipment mentioned above is a very useful technique in observing the kind of decomposition, fragmentation mechanism, phase changes, and mass loss depending on structure–stability relationships. The influence of ionic radii, acceptor properties of the metal atoms, and their electronegativity values are correlated with the thermoanalytical data and the route of decomposition. Representative experimental results of our investigations are included for comparison.

INTRODUCTION

The thermal behaviour and fragmentation patterns of metal complexes with β-diketones as ligands have been discussed by several authors [4–7] but none has used the equipment described in the present work. The β-diketonates listed in Table 1 were analyzed for purity and identified by IR spectroscopy before the TG–DTA–MS experiments were carried out. The thermal properties of these compounds have become of particular interest for some practical applications, e.g. in gas chromatography [8].

In an attempt to obtain further information about the thermal degradation we compared the temperatures of endothermic and exothermic phenomena with mass loss and composition of the volatile release. The coupling system TG–DTA–MS was found to be especially suited to the investigation of particular decomposition mechanisms.

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TABLE 1

Series of metal acetylacetonates and their abbreviations

Compound	Abbreviation
Bis(acetylacetonato)cadmium(II)	$Cd(acac)_2$
Bis(acetylacetonato)iron(II)	$Fe(acac)_2$
Bis(acetylacetonato)cobalt(II)	$Co(acac)_2$
Bis(acetylacetonato)copper(II)	$Cu(acac)_2$
Bis(acetylacetonato)manganese(II)	$Mn(acac)_2$
Bis(acetylacetonato)nickel(II)	$Ni(acac)_2$
Bis(acetylacetonato)zinc(II)	$Zn(acac)_2$

EXPERIMENTAL

Apparatus

For the TG–DTA–MS experiments, a coupling system Netzsch STA 429 simultaneous thermoanalyzer and a Balzers QMG 511 quadrupole mass spectrometer were used. A quadrupole system has been selected as an analyzer for the investigation of mass distribution in the gas atmosphere. The simple and space-saving construction of a quadrupole mass filter, and the sufficient resolving capacity, even at a rapid mass scan, render the quadrupole mass spectrometer well suited for combination with a thermoanalyzer.

A Balzers mass filter was used for the mass range 1–511, with variable operating possibilities via a digital electronic control system. The mode of operation can be described as follows:

(1) in the mass range of interest, up to 12 fixed mass units (m/z) can be registered simultaneously with respect to their dependence on the temperature with an optimum selected sensitivity;

(2) a pre-selected mass range can be scanned once or repeatedly with scan speeds between 0.1 ms/mass unit and 30 s/mass unit.

The coupling interface between the thermoanalyzer and the mass spectrometer fulfils two functions: it operates simultaneously as a gas inlet system for the quadrupole mass filter, and as a pressure reduction system, if the pyrolytic decomposition of a sample occurs in a gaseous atmosphere.

The coupling system between Netzsch DTA STA 429 with a Balzers mass spectrometer consists of a two-stage gas inlet system, an arrangement of orifices arranged in Al_2O_3 tubes. The experimental conditions and procedure have been described elsewhere [1–3]. Certain details of individual tests are included in the text.

Materials

Analytically pure reagents were used for the preparation of the metal acetylacetonates.

RESULTS AND DISCUSSION

TG–DTA investigations

The DTA curves of all the compounds investigated exhibit similar broad exotherms attributed to the oxidative decomposition of the metal complexes, depending on their thermal stability. Accordingly, it is assumed that the temperature interval of the predominant decomposition reaction and mass loss is a measure of complex stability. The temperature intervals mentioned above are shown in Table 2.

The values between 100 and 346 K are arranged in increasing order and represent the stability rule for divalent transition metal chelates as established by Irving and Williams [9], with the exception of Cu(acac)$_2$: Cu > Zn > Ni > Co > Fe > Mn. The unusual behaviour of the copper chelate has already been reported by Liptay [13], dealing with the application of thermal analysis in complex chemistry. The TG–DTA curve (Fig. 1) of Mn(acac)$_2$ is chosen as a typical example of all the metal chelates investigated. Exactly three exothermic peaks arise in the temperature range 273–623 K, with increasing peak height from the first to the third peak (peak maxima at 313, 552 and 602 K).

The volatility of metal-β-diketonates as a function of ionic radii has been described by Sievers [10]. Increasing volatility occurs with decreasing ionic radii. In connection with this report an attempt was made to explain the thermal stability of the metal chelates concerning this relationship. Figure 2 presents the dependence of thermal decomposition on the ionic radii of the metal ions.

The negative slope of the graph indicates increasing thermal stability with decreasing values for the ionic radii following the well-known Irving–Williams rule.

An analogous correlation can be made regarding electronegativity [11] and acidity of the transition metal ions, by attracting forces with donor atoms of

TABLE 2

Temperature intervals of mass loss of metal acetylacetonates

Metal	Cu(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Zn(II)
ΔT(K)	100	132	243	290	331	346

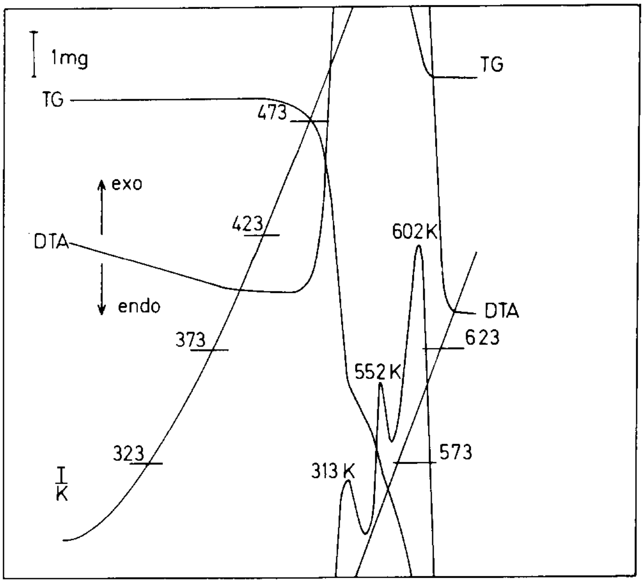

Fig. 1. TG–DTA curve for Mn(acac)$_2$.

β-diketones as ligands (see Fig. 3). This means that the inreasing bonding strength of the metal–oxygen bond is indicated by higher values for the temperature intervals of metal complex decomposition.

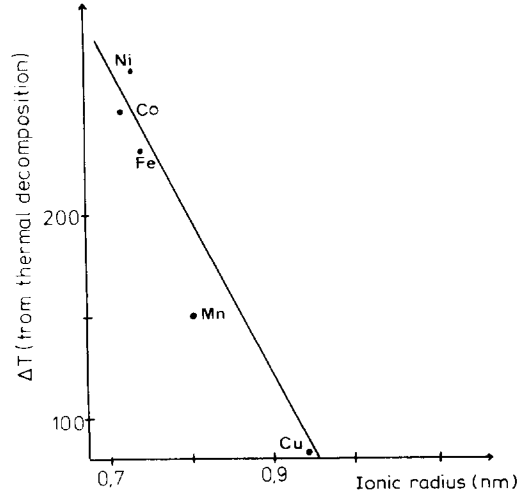

Fig. 2. Correlation of decomposition temperature ranges given by DTA curves with the ionic radii of the metal ions.

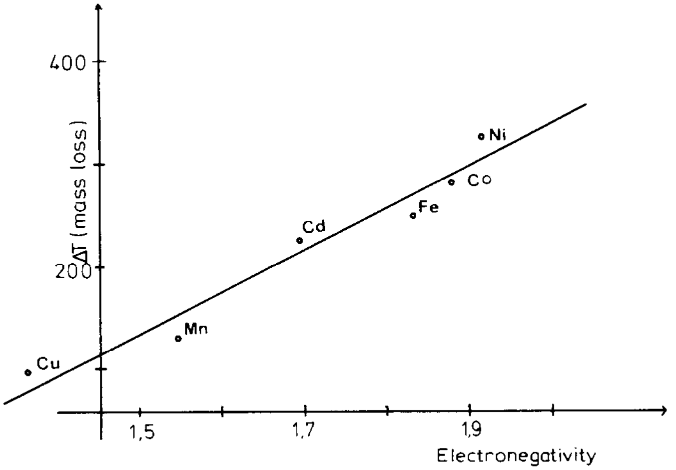

Fig. 3. Correlation between temperature range of mass loss in metal complex decomposition and the electronegativity of the transition metals.

MS-investigations

Corresponding to the thermoanalytical data given by the TG–DTA curve from Mn(acac)$_2$, the degradation process of this compound will be discussed and general conclusions for the chelates of other metals should be made. Typical fragmentation patterns for metal acetylacetonates have been de-

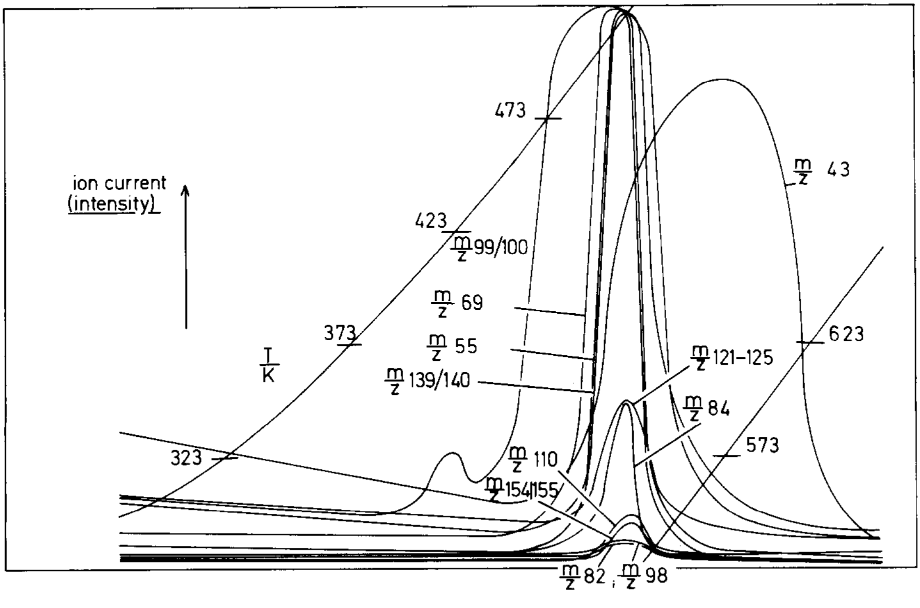

Fig. 4. Variation of intensity for selected mass units from the fragmentation of Mn(acac)$_2$.

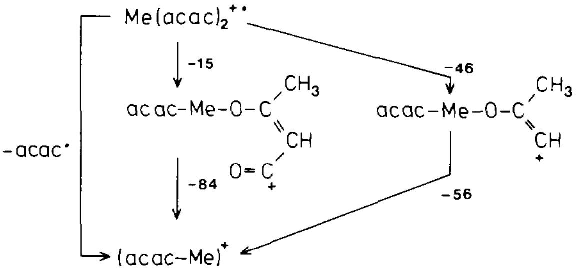

Fig. 5. Fragmentation pattern of metal acetylacetonates.

scribed by Westmore [7] and MacDonald and Shannon [12]. In connection with these results the sequence of the fragmentation of the metal complexes as a function of temperature was investigated using the special instrumental equipment of the mass spectrometer. As an alternative to recording normal mass spectra it is possible to examine the ion currents of 12 different mass ranges or mass units. The temperature dependence of the intensity of some characteristic mass units is shown in Fig. 4.

The spectrum was registered in the temperature range 293–673 K. At 415 K the intensity of the mass $m/z = 99$ exhibits a first maximum due to the elimination of the complete ligand. Further fragmentation of the ligand is indicated by a second maximum at 513 K. At this temperature the intensities of the ligand as well as all selected mass units representing the typical degradation of this complex show a common maximum.

The intensity of $m/z = 43$ due to loss of CH_3CO from the ligand exhibits a third maximum at 602 K and indicates fragmentation of the second ligand. At exactly this temperature the DTA curve shows the third exothermic peak corresponding to the third step of oxidative decomposition. A general fragmentation pattern is exhibited in Fig. 5, without showing the change of a unit in valency of the metal ion, according to the results of other authors [7,11].

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