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THERMAL DECOMPOSITION STUDY ON NICKEL(II)– AND COBALT(II)–β-DIKETONATE LEWIS-BASE ADDUCTS BY SIMULTANEOUS TG–DTA–MS ANALYSIS

K.-H. Ohrbach, G. Radhoff and *A. Kettrup*+

UNIVERSITÄT-GH PADERBORN, WARBURGER STRASSE 100,
D-4790 PADERBORN, G.F.R.

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Analytically pure nickel(II)– and cobalt(II)–acetylacetonate were used to prepare several addition compounds with Lewis-bases (2-picoline-N-oxide, 4-picoline-N-oxide, pyridine-N-oxide) in order to investigate their thermal stability in oxidative atmospheres. Comparison of the thermoanalytical TG–DTA data of the chelates with those on the adducts showed similarities in thermal degradation. A fragmentation pattern observed on simultaneous mass spectrometric investigation is discussed. Elimination of ligand or base molecules corresponding quantitatively to the estimated mass loss values from the TG-curves has been demonstrated.

Investigations of the thermal stability of organometallic substances have been reported [1, 2].

Simultaneous TG–DTA–MS measurements are well suited to the study of time–temperature-dependent decompositions and mass spectrometric identification of the degradation products up to 1770 K.

Experimental

Experimental procedures and conditions have been described earlier [3–6].

The Lewis-base adducts were obtained by recrystallizing Ni(II)– and Co(II)–acetylacetonates in methanolic solutions of the bases. The precipitates were isolated, washed with ether and vacuum-dried for 4 hours at 60°.

Results and discussion

Heating the addition complexes of cobalt– and nickel–acetylacetonate with various organic bases (see Table 1) leads to similar thermal degradations, as shown by the course of the TG–DTA curves.

Table 1

Compound	DTA peak temperatures, K endotherm T_p	 exotherm T_p	 exotherm T_p
$Co(acac)_2(2\text{-picNO}) \cdot 4\,H_2O$	393	468	553
$Co(acac)_2(4\text{-picNO}) \cdot 3\,H_2O$	373	468	555
$Co(acac)_2(pyNO)_4 \cdot H_2O$	395	473	563
$Ni(acac)_2(2\text{-picNO}) \cdot 2\,H_2O$	428	468	628
$Ni(acac)_2(4\text{-picNO}) \cdot 3\,H_2O$	365	468	630
$Ni(acac)_2(pyNO)_4$	–	461	608

Abbreviations: acac = acetylacetonate, 2-picNO = 2-picoline-N-oxide, 4-picNO = 4-picoline-N-oxide, pyNO = pyridine-N-oxide, T_p = endothermic (exothermic) peak temperature.

The following sequence of complex stability is given by the increasing endothermic peak temperatures due to the compounds melting.

$$Ni(acac)_2(2\text{-picNO}) > Co(acac)_2(pyNO)_4 > Co(acac)_2(2\text{-picNO}) >$$
$$> Co(acac)_2(4\text{-picNO}) > Ni(acac)_2(4\text{-picNO})$$

The compound $Ni(acac)_2(pyNO)_4$ undergoes exothermic oxidative decomposition in air without melting.

All DTA curves exhibit two endothermic peaks, accompanied by a two-stage mass loss curve.

During our mass spectrometer runs in the temperature range of the first peak of the DTA curves the following fragment ions arise from the β-diketone:

$m/z = 58 / CH_3COHCH_2$

$m/z = 84 / CH_3COCHCO$

$m/z = 99 / CH_3COCHCOCH_3$

and also

$m/z = 109$ / picNO

$m/z = 94$ / pyNO

$m/z = 79$ / py

$m/z = 52 / C_4H_4$

corresponding to the loss and fragmentation of base molecules.

Figure 1 shows as an example the mass spectrum of $Ni(acac)_2(2\text{-picNO})$ in the temperature range from 475 to 495 K.

The thermal behaviour of $Co(acac)_2(pyNO)_4$ will be discussed as typical for all adducts listed in Table 1. Figure 2 shows the TG–DTA curves of this complex.

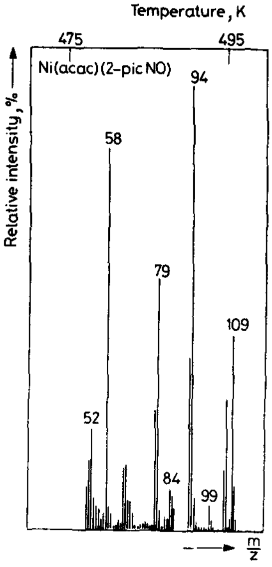

Fig. 1 Mass spectrum of Ni(acac)$_2$(2-picNO)

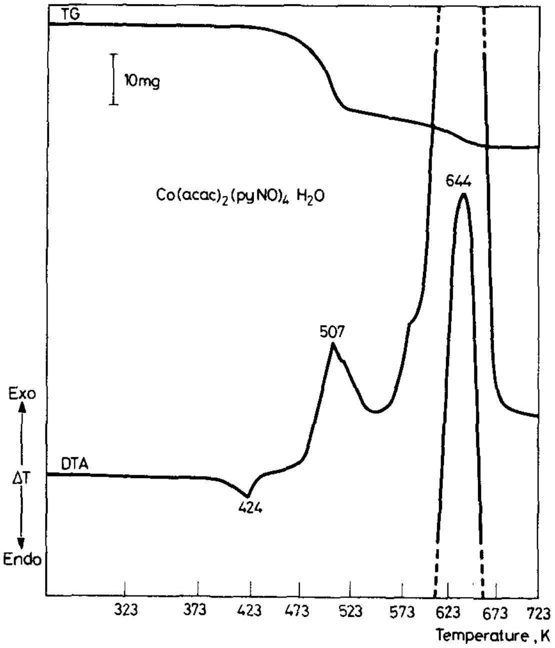

Fig. 2 TG–DTA curves of Co(acac)$_2$(pyNO)$_4$ • H_2O

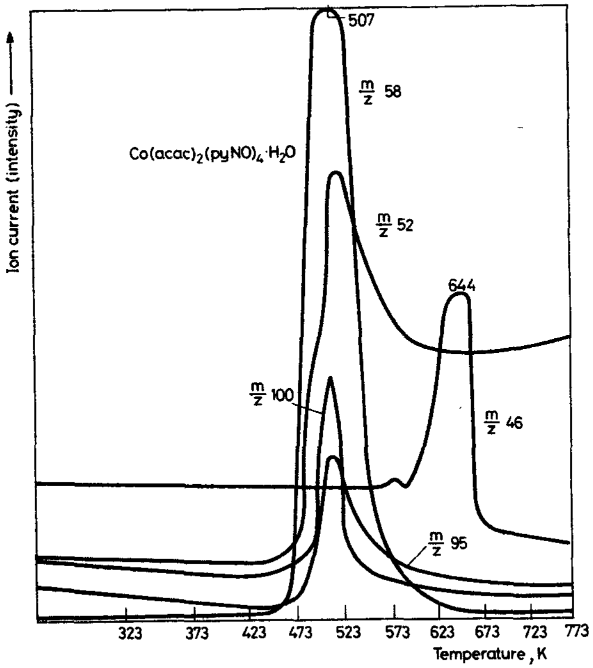

Fig. 3 Intensities of selected ion currents of $CO(acac)_2(pyNO)_4 \cdot H_2O$

The endotherm in the DTA curve shows melting of the compound at a peak temperature of 424 K, followed by two exothermic peaks, at 507 and 644 K, caused by loss of oxidative products; this is indicated by a total mass loss of 82.2% in the TG curve, via a two-stage mechanism.

Simultaneous recording of the intensities of different ion currents with

$m/z =$ 46 / NO_2
$m/z =$ 52 / C_2H_4
$m/z =$ 58 / CH_3COHCH_2
$m/z =$ 95 / pyNO
$m/z =$ 100 / $CH_3COCH_2COCH_3$

in the temperature range from 293 to 723 K allows individual steps in the exothermic degradation of $Co(acac)_2(pyNO)_4$ to be correlated with the appearance of typical fragment ions, as shown in Fig. 3.

The first peak in the DTA curve corresponds to a maximum intensity of ion currents with m/z values of 52, 58, 95 and 100 (loss of base as well as loss of ligand molecules). Therefore, conclusions relating to the strengths of the metal-ligand or metal-base bonds cannot be drawn. The course of the ion current with $m/z = 46$ / NO_2 is therefore not significant for the first loss of base or ligand, and hence the stability of the addition compound.

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Zusammenfassung — Die thermische Stabilität verschiedener Additionskomplexe des Nickel(II)— und des Kobalt(II)—acetylacetonats mit organischen Lewis-Basen (2-Picolin-N-oxid, 4-Picolin-N-oxid und Pyridin-N-oxid) wurde in oxidativer Atmosphäre untersucht. Zur Darstellung der Addukte wurden die Acetylacetonate analysenrein eingesetzt.

Ein Vergleich der thermischen Analysendaten (TG—DTA) der Chelate mit denen der Addukte zeigt einige Parallelen im thermischen Abbau. Anhand von simultan aufgenommen Massenspektren wird ein Fragmentierungsschema aufgestellt und diskutiert. Die Abspaltung eines Ligandmoleküls beziehungsweise eines Moleküls der Base aus dem Addukt konnte aus dem Massenspektrum belegt werden und entspricht quantitativ den aus den TG-Kurven bestimmen Gewichtsverlusten der Addukte.

Резюме — Аналитически чистые ацетилацетонаты двухвалентных никеля и кобальта были использованы для получения нескольких аддуктов с такими льюисовскими основаниями как N-окись пиридина и N-окиси 2- и 4-пиколина, с целью исследования их термоустойчивости в окислительной атмосфере. Сравнение ТГ—ДТА данных для хелатов и их аддуктов, свидетельствует о подобии их термического разложения. Обсуждена также их фрагментация, наблюдаемая совмещенным масс-спектрометрическим методом. Выделение молекул лиганда или основания количественно соответствовало значениям потери веса, установленным из ТГ-кривых.