Preparation and reactivity of metal-containing monomers.

36. Thermal stability of methacryloylacetonates and polymethacryloylacetonates of transition metals

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The thermal decomposition of Cu^{II}, Co^{II}, Ni^{II}, Mn^{II}, Fe^{III}, and Cr^{III} methacryloylacetonates has been compared with the thermal behavior of the corresponding acetylacetonates and poly(methacryloylacetonates). Dehydration and thermal polymerization of methacryloylacetonates occur at 110—160 °C. The results of the thermolysis conform with the Irving—Williams sequence for the stability of the complexes of bivalent transition metals. Thermal destruction of metallopolymers differs from that of low-molecular analogs. The temperature of complete decomposition of the compounds studied correlates with the number of electrons in the d-orbital of the metal.

Key words: thermal decomposition, metal-containing monomers, metallopolymers, methacryloylacetonates, poly(methacryloylacetonates), acetylacetonates, transition metals.

Investigation of the thermal properties of metal-containing monomers of the chelate type is of interest, first, for producing metal-containing polymeric coatings by the sublimation of the corresponding metal-containing monomers. Second, the study of thermal polymerization of these monomers in the condensed phase is significant for itself. Thermal transformations of diacrylates have been studied previously[1,2], and it has been shown that their thermal decomposition is accompanied by the formation of polymeric products, which occurs by a radical mechanism. In the present work we have compared the thermal decomposition of acetylacetonates and methacryloylacetonates ($(MAc)_nM$) as well as poly(methacryloylacetonates) of Cu^{II}, Co^{II}, Ni^{II}, and Mn^{II}.

Experimental

Transition metal acetylacetonates were prepared and purified by the known procedures.[3] The synthesis of methacryloylacetonates has been described previously.[4] Polymerization of their alcoholic solutions was carried out in an inert atmosphere in sealed ampules through the action of azoisobutyronitrile. The precipitate was washed many times with methanol and dried to constant mass. The complex thermal investigation was carried out on a C derivatograph (MOM, Hungary) in air, the rate of heating was 5—10 °C min^{-1} over the temperature range 20—600 °C. The calibration was based on the melting points of In and Sn (429.8 and 504.9 K, respectively). The weight of the sample was 50 mg. The activation energy was calculated by the method of digital simulation.[5] The thermal effect of the thermolysis of chelates was determined by the digital simulation method from the magnitude of the exothermic effect for the corresponding temperature interval. X ray diffraction patterns of the powders were obtained on a DRON-UM-2 diffractometer using Cu-Kα radiation. The IR spectra were recorded on an UR-20 spectrophotometer. The samples were prepared as suspensions in vaseline oil.

Results and Discussion

The complex character of the decomposition of the methacryloylacetonates of the series I transition metals cannot be explained from the normal sequence of the stability of complex compounds of these elements (Mn < Co < Ni < Fe).[6] In some cases chemical transformations in a sample subjected to pyrolysis directly follow physical processes, for example, melting. These transformations occur over a relatively wide temperature range; the superposition of the heats of these transformations hampers the interpretation of the destruction curves in dynamic studies. Therefore, to facilitate the

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analysis of the experimental results, we compared the character of the thermal decomposition of methacryloylacetonates with the data for their simplest analogs, acetylacetonates.

Unlike acetylacetonates, which lose coordinated water in the temperature range 70—100 °C,[7] methacryloylacetonates are dehydrated between 110 and 160 °C. (It has been reported[8] that dehydration of some chelates occurs at even higher temperatures, 150—200 °C.) However, at these temperatures polymerization of metal-containing monomers probably takes place, and the endothermic effect of the elimination of water molecules is overriden by the greater exothermic effect of polymerization.

Methacryloylacetonates of transition metals sublimate already at 55—70 °C, *i.e.*, at considerably lower temperatures than acetylacetonates (120—160 °C). At the same time, the M—O bond in unsaturated chelates is stronger than that in saturated chelates.[4] In fact, the maximum heat evolution on the DTA curves (Figs. 1, 2), which indicates partial decomposition of methacryloylacetonates, is 50 °C higher than that for the corresponding acetylacetonates, and the temperature of the complete thermal destruction, after which the mass of

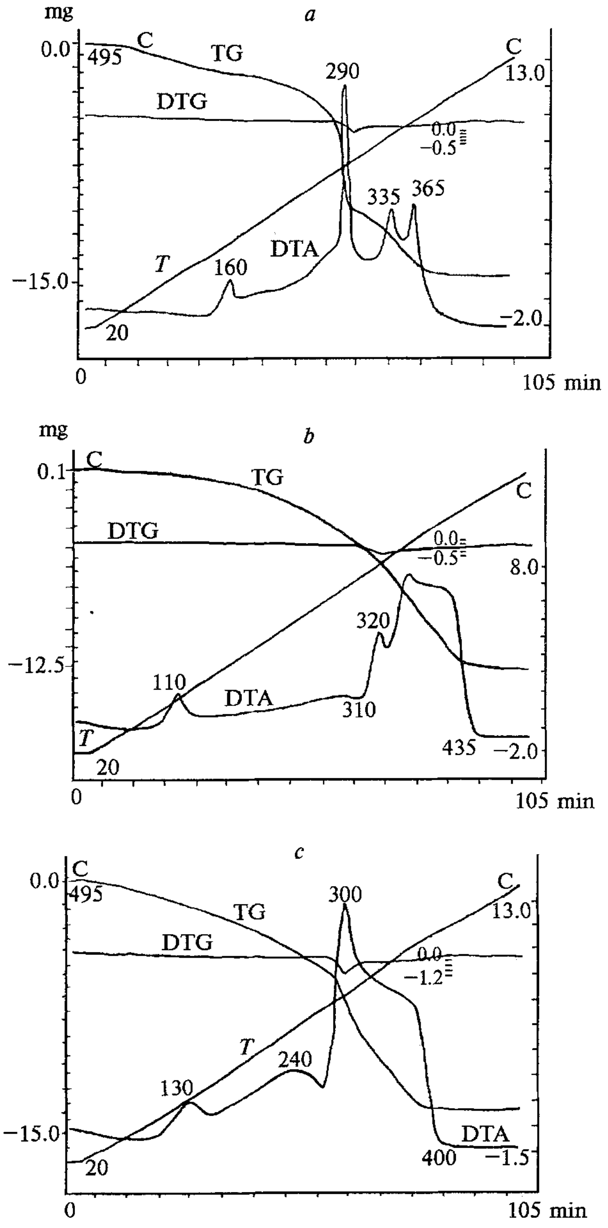


Fig. 1. Derivatograms of methacryloylacetonates of Ni^{II} (*a*); Co^{II} (*b*); Mn^{II} (*c*).

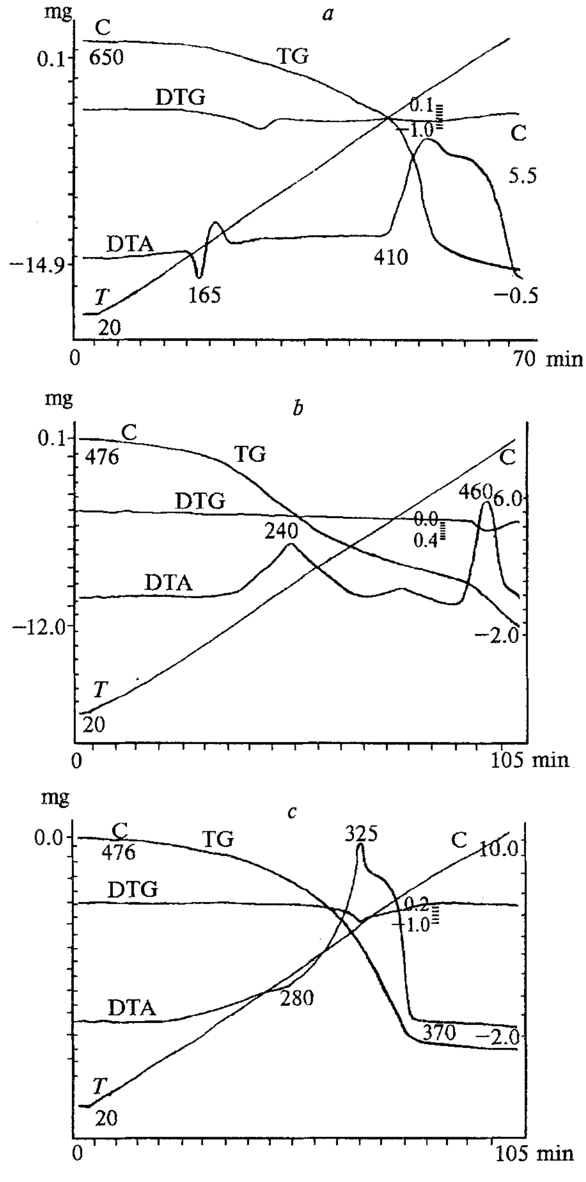
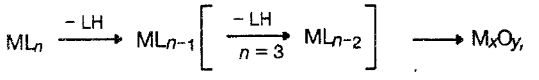


Fig. 2. Derivatograms of methacryloylacetonates of Cu^{II} (*a*) (the rate of heating was 10 °C min^{-1}); Fe^{III} (*b*); Cr^{III} (*c*).

the sample no longer changes, is 50—100 °C higher. The total mass loss over the temperature range considered amounts to 75—85 %.

Decomposition of metal methacryloylacetonates probably begins with the abstraction of one methacryloylacetone molecule. A mass loss of 29—40 % on the TG curve corresponds to this process. Similar thermal destruction has been observed for acetylacetonates.[7] The intermediate chelates are unstable and are hydrolyzed in air. According to the data from X-ray phase analysis, the final products of thermolysis are metal oxides. In general form, the thermal decomposition of methacryloylacetonates may be represented by the following scheme:



$$ML_n \xrightarrow{-LH} ML_{n-1}\left[\xrightarrow[n=3]{-LH} ML_{n-2}\right] \longrightarrow M_xO_y,$$

where $L = CH_2{=}C(Me)C(O^-){=}CHCOCH_3$; $n = 2$, $x = y = 1$; $n = 3$, $x = 2$, $y = 3$.

The results of a complex thermal investigation of $(MAc)_2Ni \cdot 2H_2O$ (Fig. 1, *a*) show that in the temperature range 60—280 °C the sample smoothly loses mass (10 %), which corresponds to the abstraction of two molecules of water of crystallization. The minor exothermic effect with a maximum at 160 °C is probably associated with polymerization (*cf.* Ref. 7). The exothermic effect at 290 °C is accompanied by a substantial loss of mass (37 %). The results of the elemental analysis imply that at this stage of the thermal destruction one ligand molecule is lost. Subsequent heating (exothermic effects with maxima at 335 °C and 365 °C) results in the complete decomposition of the complex. The final product of thermolysis is the cubic NiO, according to X-ray phase analysis.[9]

In the case of cobalt methacryloylacetonate (Fig. 1, b) the smooth loss of mass begins at 70 °C. The exothermic effect with a maximum at 110 °C apparently characterizes the thermal destruction of the metal-containing monomer. In the same region the loss of two molecules of water of crystallization occurs (10.2 %), as in the case of the nickel chelate. A drastic loss of mass (36 %) accompanied by the evolution of a great amount of heat is exhibited as an exothermic effect with the maximum at 320 °C indicates the partial destruction of the chelate to evolve one methacryloylacetone molecule. According to the data of IR spectroscopy, the intermediate product, cobalt monomethacryloylacetonate, retains the chelate structure; it is hydrolyzed in air. In the region between 355 °C and 435 °C the complex completely decomposes and no further change in the mass is observed.

The character of the decomposition of manganese methacryloylacetonate (Fig. 1, *c*) is similar to the above-described character of the destruction of Ni^{II} and Co^{II} complexes. Sublimation begins at 60 °C. The exothermic effect at 130 °C is probably associated with thermal polymerization. The heat evolution at 240 °C corresponds to the elimination of one ligand molecule accompanied by a strong exothermic effect in the DTA curve and by the loss of 37.2 % of the sample mass. The IR spectrum for the resulting compound is similar to that for cobalt monomethacryloylacetonate; this attests to retention of the chelate structure. In the region between 280 °C and 400 °C the exothermic effect associated with the complete decomposition of the compound is observed.

Anhydrous copper chelate (Fig. 2, *a*) possesses the highest thermal stability among all of the methacryloylacetonates studied: no change in the mass occurs up to 165 °C. The slight endothermic effect observed at this temperature corresponds to the melting of the complex (*cf.* Ref. 4). During further heating of the sample a smooth loss of mass occurs (38 %), which results from the destruction of the chelate unit. The final product of the thermolysis is CuO of the cubic modification,[9] as shown by X-ray phase analysis.

A thermographic study of the iron complex (Fig. 2, *b*) showed that in the temperature region between 20 °C and 500 °C two exothermic effects with maxima at 240 °C and 460 °C are exhibited. The former effect is accompanied by the smooth loss of 29.1 % of the sample mass and corresponds to the abstraction of one ligand molecule. The latter effect is associated with the complete decomposition of the sample. The final products of the thermolysis (up to 500 °C) are Fe_2O_3 and α-Fe_2O_3, as confirmed by X-ray phase analysis.[9]

The analysis of the thermogram of chromium *tris*-methacryloylacetonate showed that the loss of mass begins at 90 °C. In the range 280—370 °C substantial mass loss (85 %) occurs with the exothermic effect maximum at 325 °C (as can be seen in Fig. 2, *b*).

Comparing the course of the thermal destruction of transition metal methacryloylacetonates with that of acetylacetonates of the same metals, one may note that the thermal stability of the former increases in the following order:

$$Fe^{III} < Mn^{II} < Co^{II} < Cr^{III} < Ni^{II} < Cu^{II}$$

and that of the latter increases in the order:

$$Mn^{II} < Fe^{III} < Co^{II} < Ni^{II} < Cu^{II} < Cr^{III}$$

These data are in good agreement with the Irving—Williams stability sequence for the complexes of series I bivalent transition metals.

Since one of the steps of the thermal decomposition of methacryloylacetonates is their polymerization, we studied the thermal stability of poly(methacryloylacetonates) of the corresponding metals for comparison. The DTA data obtained in air show that the course of thermal destruction of the polymers differs somewhat from that of their low-molecular analogs. Polymerization of methacryloylacetonates may be accompanied by weakening of the M—O bond in the chelate unit, which results in a decrease in the temperature of the onset of decomposition of the polymers, as compared with that of the metal-containing monomers, by 100—150 °C. The absence of a complex exothermic peak in the DTA curve for poly(metacryloylacetone) (PMAc) not containing a metal confirms our suggestion that the peak observed in the thermolysis of macrocomplexes characterizes the thermal effect from the destruction of the chelate ring. The major loss of mass of Cu^{II}, Ni^{II}, Co^{II}, and Mn^{II} poly(methacryloylacetonates) occurs above 240 °C and is accompanied by great heat evolution. On the basis of their thermal stability, macrochelates can be positioned in the following sequence:

$$\text{PMAc} < \text{Cu} < \text{Ni} < \text{Co} < \text{Mn}.$$

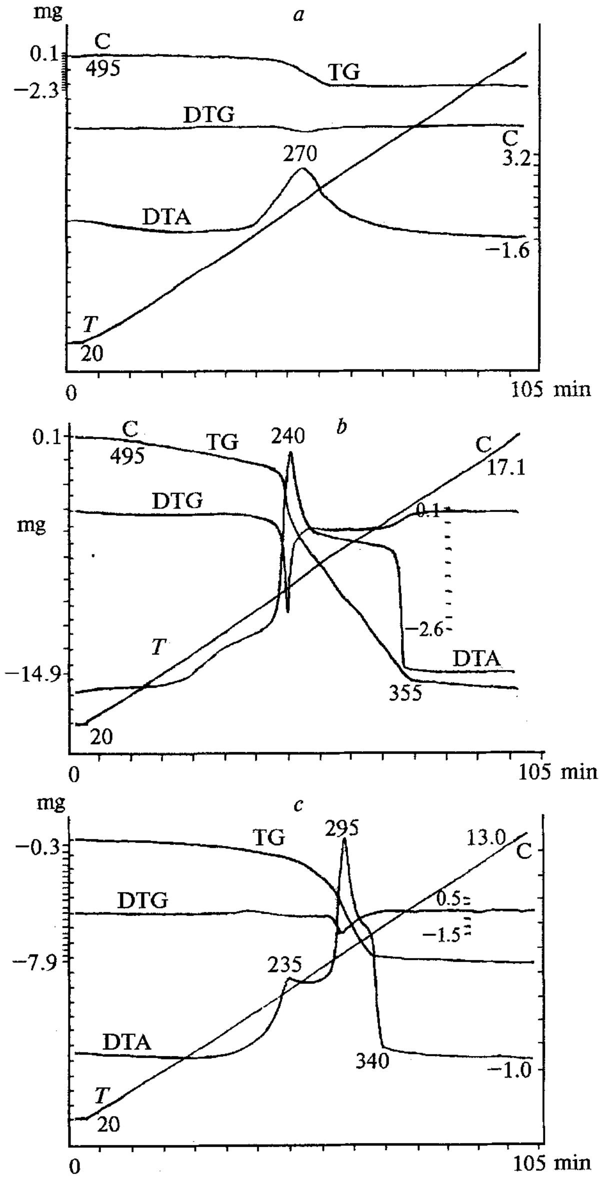


Fig. 3. Derivatograms of poly(methacryloylacetonates) of Cu^{II} (*a*); Co^{II} (*b*), Ni^{II} (*c*).

Copper poly(methacyloylacetonate) (Fig. 3, *a*) is stable up to 240 °C.

During further heating an exothermic effect with a maximum at 270 °C accompanied by a loss of sample mass (40.5 %) is observed. This corresponds to the thermal destruction of the polymer. The final product of the thermolysis, as in the case of the monomeric chelate, is the cupric oxide in the cubic modification as shown by X-ray phase analysis.[9]

The TG curve for cobalt macrochelate (Fig. 3, *b*) exhibits the smooth loss of mass of the sample (10 %) in the region between 40 °C and 220 °C, which is not accompanied by thermal effects. Thermal destruction of the macromolecule occurs in the interval 220—355 °C with a mass loss of 41 %.

Nickel poly(metacryloylacetonate) (Fig. 3, *c*) is thermally stable up to 225 °C. Upon further heating, destruction of the macromolecule occurs in the range 230—340 °C with the loss of 40.1 % of mass, which is exhibited as two exothermic effects with maxima at 235 °C and 295 °C.

The polymeric chelate of manganese (Fig. 4, *a*) sublimates smoothly up to 235 °C. In the range 240—360 °C destruction of the polymer with substantial

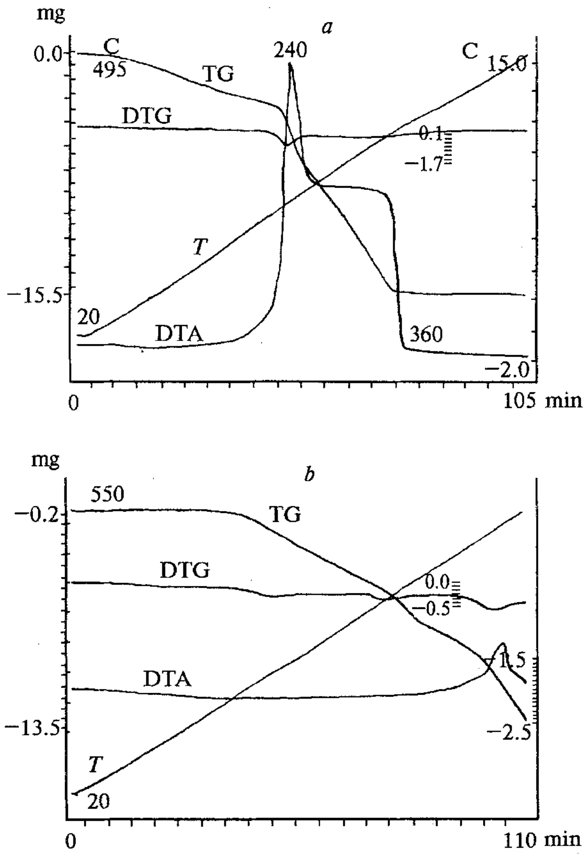


Fig. 4. Derivatograms of Mn^{II} poly(methacryloylacetonate) (*a*) and poly(methacryloylacetone) (*b*).

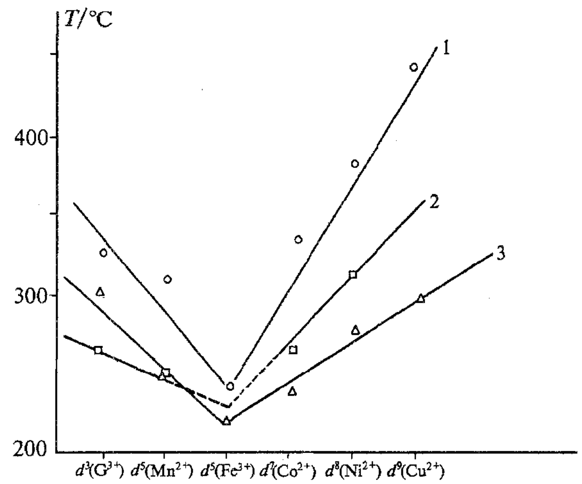


Fig. 5. The temperatures of decomposition of transition metal methacryloylacetonates (*1*), poly(methacryloylacetonates) (*2*), and acetylacetonates (*3*).

mass loss (42 %) occurs to afford a product which is stable when heated to 500 °C.

Poly(methacryloylacetone) is thermally stable up to 205 °C (Fig. 4, *b*). At higher temperatures the macro ligand begins to lose mass smoothly; as this takes place, the DTA curve does not exhibit any changes in the energy of the system. Starting at 205 °C, the smooth loss of mass is recorded on the TG curve, which occurs up to 500 °C. Thus, the non-coordinated polymer possesses lower thermal stability than the metal-containing derivatives.

As shown in Fig. 5, Cu^{II} chelates and Cr^{III} acetylacetonate are the most stable, while Fe^{III} complexes possess the lowest stability. Interestingly, an extreme dependence of T_d on the number of electrons in the d-orbital of the metal with a minimum at d^5 Fe^{III} is observed, which has not yet been explained.

A similar dependence between the decomposition temperature of metal chelates and the properties of the central atom (atomic number, electronegativity, ionization potential) has been observed previously[10,11] for complexes of poly(8-hydroxy-7,5-divinylquinoline).

An examination of the data on the kinetics of thermal decomposition made it possible to estimate the rate constants and activation energies (E_a) of thermal destruction (Table 1) from the equation given below:[12]

$$da/dt = K_0 e^{-E_a/RT} \cdot f(\alpha),$$

where K_0 is the pre-exponential function and α is the degree of conversion.

As the data of Table 1 indicate, the effective activation energy of thermal destruction of the complexes under consideration increases in the following order of ligands.

MAc < Hacac < PMAc

Table 1. Thermodynamic and kinetic data on thermal destruction of transition metal methacryloylacetonates, poly(methacryloylacetonates), and acetylacetonates

Compound	Effective activation energy /kJ mol^{-1}	The reaction order	Q/J g^{-1}
$(MAc)_2$ Cu	14.3	2	8903
$(MAc)_2$ Co · 2H O	25.6	1	14545
$(MAc)_2$ Ni · 2H O	39.1	1	11646
$(MAc)_2$ Mn · 2H O	34.2	1	15768
$(MAc)_3$ Fe	8.3	0.5	4546
$(MAc)_3$ Cr	18.7	1	1336
PMAc	57.9	1	—
$(MAc)_2$ Co	92.6	2	18468
$P(MAc)_2$ Ni	138.8	1	17998
$P(MAc)_2$ Mn	149.3	2	21052
$P(MAc)_2$ Cu	62.9	1	2198
$(acac)_2Cu$	62.9	1	5858
$(acac)_2Co \cdot 2H_2O$	112.2	2	6678
$(acac)_2Ni \cdot 2H_2O$	110.8	1	8712
$(acac)_2Mn \cdot 2H_2O$	116.7	2	8159
$(acac)_3$ Fe	29.3	1	9943
$(acac)_3$ Cr	83.2	1	1336

In turn, E_a as a function of the nature of the transition metal increases for these complexes in the following order

MAc: $Fe^{III} < Cu^{II} < Cr^{III} < Co^{II} < Mn^{II} < Ni^{II}$
acac: $Fe^{III} < Cu^{II} < Cr^{III} < Ni^{II} \approx Co^{II} < Mn^{II}$
PMAc: $Cu^{II} < Co^{II} < Ni^{II} < Mn^{II}$

and varies over the range (kJ mol^{-1}): MAc 2—9, AA 7—26, and PMAc 15—35.

It should be noted for comparison that E_a for poly(5,5'-methylene-bis-salicylaldehyde—4,4'-diaminodiphenyl ether) and macro complexes amounts to 15—23 kJ mol^{-1} (see Ref. 12) and increases in the following order of transition metals:

$Co^{II} < Ni^{II} < Cu^{I} < Mn^{II}$.

A comparison of the effective amount of heat evolved during the destruction of the chelate unit (Q) shows that it increases in the following order of chelating ligands: Hacac < PMAc < MAc, and in the following order of metals:

acac: $Cr^{III} < Cu^{II} < Co^{II} < Mn^{II} < Ni^{II}$
PMAc: $Cu^{II} < Co^{II} < Mn^{II} < Ni^{II}$
MAc: $Cr^{III} < Fe^{III} < Cu^{II} < Ni^{II} < Co^{II} < Mn^{II}$.

The peculiarities revealed probably result from the different stabilities of the chelates being compared.

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