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THE THERMAL BEHAVIOUR OF SOME Co(II) COMPLEX COMBINATIONS WITH SCHIFF BASES

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Abstract

In order to evidence the ligand influence on the thermal stability for Co(II) complex combinations, we have synthesized five complex combinations of this metal with Schiff bases obtained by condensation of ethylenediamine with acetylacetone and benzoylacetone; phenylenediamine with benzoylacetone and also anthranilic acid with benzaldehyde.

Keywords: Co(II) complex combinations, kinetic parameters, Schiff bases, thermal stability, X-ray analysis

Introduction

The ligand influence on the thermal stability of some Co(II) complex with Schiff bases was emphasized by thermal analysis.

Although these kinds of complexes are used in medicine, biology and analytical chemistry, the thermal stability studies are sporadically presented in the literature [1–2].

In this paper, we are going to present a possible correlation between the thermal stability and the structure of the Schiff bases.

Experimental

The Schiff bases and Co(II) complex synthesis were presented in another papers [3–5]. Table 1 presents the symbols, formula and molecular mass of Co(II) complexes.

The DTA, DTG, TG curves have been recorded with a Derivatograph-C type MOM (Hungary), in static air atmosphere, with a heating rate between 1.5–10 K min^{-1}. As reference material α-alumina was used. The sample masses were between 15–45 mg,

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* Dedicated to Prof. Segal on the occassion of his 70th birthday

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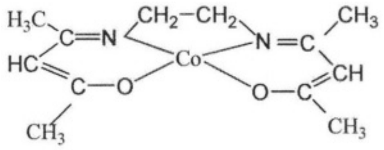
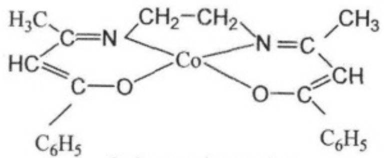
except Co(ec), for which sample mass was 6 mg. A Specord M-80 Zeiss Jena spectrophotometer allowed the IR spectra recording. The X-ray powder diffractograms were carried out by a Philips diffractometer with a copper anode.

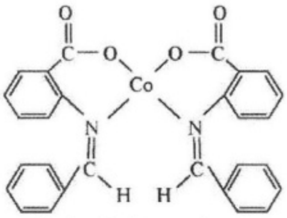
In the Fig. 1 the Co(II) combinations' structure is presented.



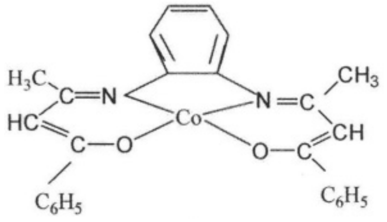
Co(ec) complex



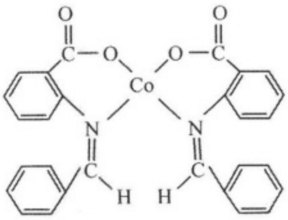
Co(benzec) complex



Co(ocabef)$_2$ complex



Co(fenbenzec) complex



Co(ocabef)$_2$ complex

Fig. 1 Co(II) combinations structure

Table 1 Information about the Co(II) combinations

No.	Symbols	Formula	mg mol^{-1}
1	Co(ec)	Co(L_1)	281
2	Co(benzec)	Co(L_2)	409
3	Co(dibenzec)	Co(L_3)	529
4	Co(fenbenzec)	Co(L_4)	512
5	Co(ocabef)	Co(L_5)	505

ec=ethylenediimino bis acetylacetone, *benzec*=ethylenediimino bis benzoylacetone, *dibenzec*=ethylenediimino bis dibenzoylacetone, *fenbenzec*=*o*-phenylenediimino bis benzoylacetone, *ocabef*=2 carboxy N-benzilydene phenylamine

Results and discussions

Thermal stability estimation

From the thermal analysis curves one can see that these are more exothermic thermal degradation processes. The thermoanalytical curves of Co(ec), Co(benzec), Co(dibenzec), Co(fenbenzec) and Co(ocabef) complex are presented in Fig. 2. These processes can be classified as follows:

A – Initiation processes of hydroperoxides forming followed by thermal decomposition and H_2O, N_2, NO elimination.

B – Carbonization processes followed by carbon residue slow oxidation. The first class processes take place at 473–573 K, and the other class at 623–873 K, except the first complex Co(ec) which presents only one rapid step, with a strong thermal effect. This special behaviour can be explained by the structure of the ligand containing only alkyl radicals – less resistant on oxidation.

The other ligands which are formed by aromatics nucleus are characterized by higher degradation temperature products. In all these case the final thermal products were CoO, Co_3O_4 and powder carbon traces (Fig. 3 and Table 2).

These data indicate for CoO and Co_3O_4, face centered cubic lattices, with unit cell parameters a(CoO)=4.257, a(Co_3O_4)=8.067 Å. Such results are in accordance with the values: a(CoO)=4.240, a(Co_3O_4)=8.072 Å corresponding to the 75–0418 and 76–1802 powder diffraction files.

The mean crystallite dimensions D_{khl}, calculated from diffraction peak at his half intensity, by Scherrer's [6, 7] relationship are: D_{200}(CoO)=355 Å and D_{220}(Co_3O_4)=415 Å.

To establish the thermal stability we have determined T_{I} (initial temperature); T_{m} (maximum temperature) and T_{f} (final temperature) corresponding the first DTA exothermic peak. The results are presented in Table 3.

From these data examination one can observe the influence of the ligand structure on these parameters.

In the passage from the first complex to the second one, we can see a characteristic temperature rising, which can be explained by apparitions of two aromatic nuclei

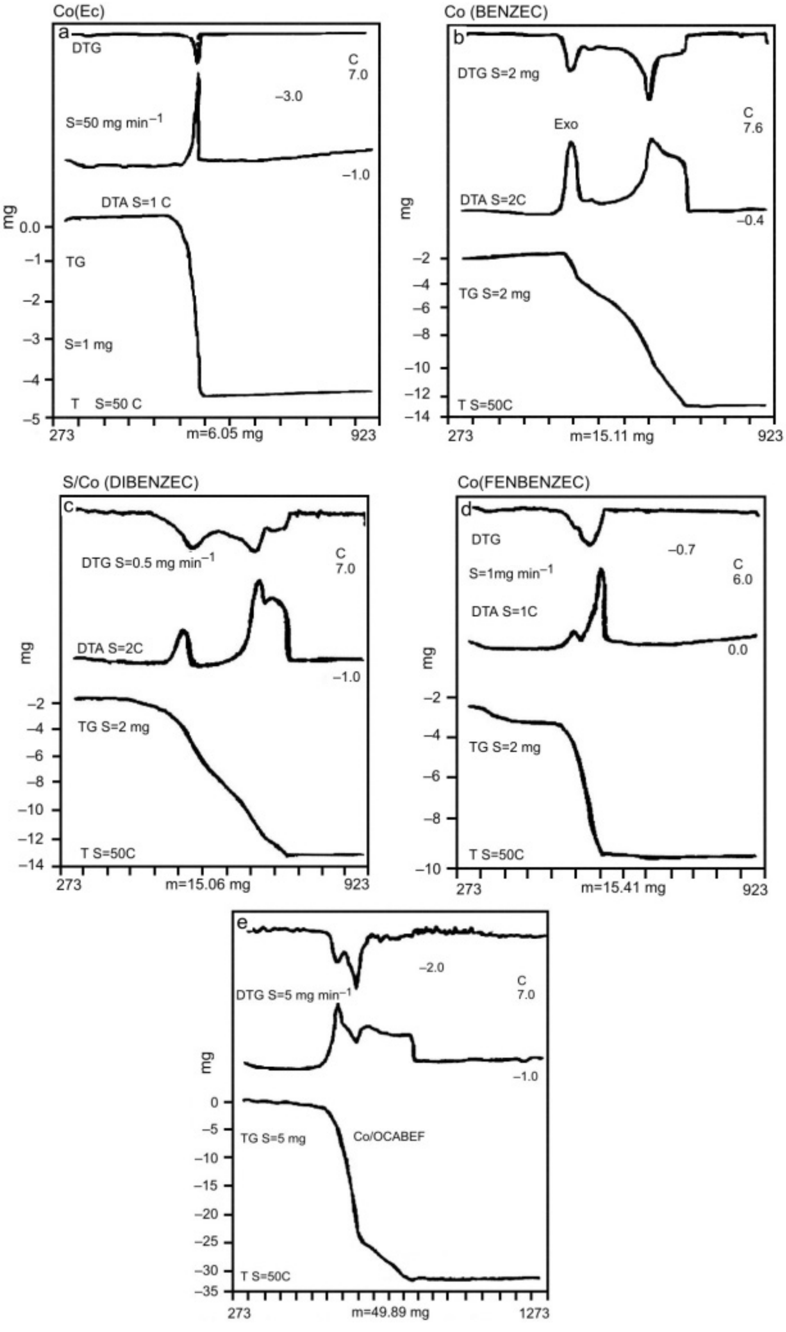


Fig. 2 Thermal curves for Co(ec), Co(benzec), Co(dibenzec), Co(fenbenzec) and Co(ocabef) complex; *S*=step of the scale

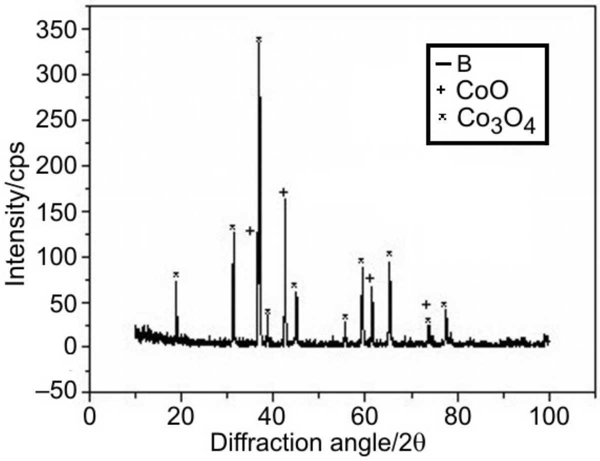


Fig. 3 X-ray diffractogram of residuum

Table 2 X-ray phase analysis of residuum. *I* – intensity of diffracted radiation; *d* – spacing of crystal planes; (*hkl*) – Miller indices; PDF – powder diffraction file

No.	*I*/cps	*d*/Å	2θ/deg	*hkl*	Phases	*PCPDF*
1.	72.5	4.656	19.044	111	CO_3O_4	76–1802
2.	125.6	2.851	31.338	220	Co_3O_4	76–1802
3.	125.9	2.457	36.539	111	CoO	75–0418
4.	322.6	2.433	36.910	311	Co_3O_4	76–1802
5.	25.9	2.328	38.629	222	Co_3O_4	76–1802
6.	162.9	2.128	42.431	200	CoO	75–0418
7.	59.6	2.017	44.894	400	Co_3O_4	76–1802
8.	83.7	1.553	59.441	511	Co_3O_4	76–1802
9.	66.7	1.505	61.535	220	CoO	75–0418
10.	87.5	1.427	65.304	440	Co_3O_4	76–1802
11.	23.3	1.284	73.678	311	CoO	75–0418
12.	37.1	1.230	77.495	533	Co_3O_4	76–1802

in Co(benzec) complex. So, we can consider that the L_2 ligand is resulting from L_1 ligand by substitution of the two methyl radicals with the two more voluminous phenyls' radicals.

Because the other two L_3 and L_4 ligands contain more aromatic nuclei we should expect a new rising of the temperature, but from the table we can see a diminishing of it. Steric hindrance presence and a less compact packing of the molecules in the crystalline network give the explanation.

For making evident the influence of the ligand structure on the T_i and T_f temperatures in Fig. 4 the variation of these parameters for Co(II) combinations is presented.

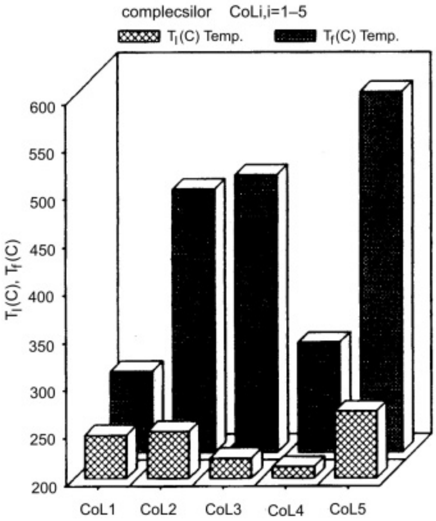


Fig. 4 The initial (T_i) and final (T_f) decomposition temperatures of Co(L_1)–CoL_5 complexes

Thermal decomposition kinetic

For these complexes one can consider two oxidative thermal decomposition stages. In the first stage: the peroxide is forming (I) and in the second one – the degradation with water elimination is happening (II).

Scheme I

Scheme II

Table 3 T_i, T_m, T_f temperatures corresponding to the first decomposition process

Compound	T_i/K	T_m/K	T_f/K
Co(ec)	520	556	558
Co(benzec)	524	563	559
Co(dibenzec)	496	538	555
Co(fenbenzec)	487	515	536
Co(ocabef)	545	602	633

The kinetic parameters have been evaluated by Flynn–Wall [8] isoconversional method using the approximate equation:

$$\ln\beta=\ln\left(\frac{ZE}{R}\right)-\ln F(\alpha)-5.331-1.052\frac{E}{RT}\qquad \alpha=\text{const.} \tag{1}$$

where Z – pre-exponential factor=$3.78\cdot10^{16}$ K min^{-1}, E – activation energy, α – conversion degree, $F(\alpha)$ – conversion function, β – heating rate.

The thermal decomposition of Co(L_1) complex was too fast even for a 1.5 K min^{-1} heating rate and for a 6 mg sample mass. In such condition a kinetic study was impossible.

The regression lines corresponding to the Eq. (1) for the decomposition of Co(benzec) complex are indicated in Fig. 5.

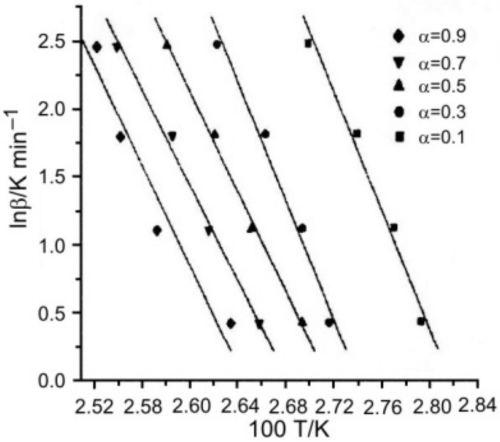


Fig. 5 The regression lines corresponding to the Eq. (1) for the decomposition of Co(benzec) complex

In the $0.1<\alpha<0.7$ decomposition range the line slope is approximately constant and the process is described by the same value of activation energy.

Table 4 Kinetic parameter values for the thermal decomposition of the Co(II) complex ($0.1<\alpha<0.7$)

No.	Symbol	n	E/kJ mol^{-1}	$\log Z/\text{s}^{-1}$	r
1.	Co(L_2)	1.0	134	14.8	0.9964
2.	Co(L_3)	0.8	112	10.5	0.9943
3.	Co(L_4)	0.9	126	13.6	0.9982
4.	Co(L_5)	1.2	183	14.4	0.9987

n – apparent order, E – activation energy, Z – pre-exponential factor, r – regression coefficient

The Co(L_4) complex with bidentate ligand presents a higher activating energy value that the other tetradentate ligands complex. This shows that the number of metal–ligand bounds influence the activation energy.

Data inspection from Tables 3 and 4, indicate some correlation between E and T_i. In previous paper [8] the linear correlation E *vs.* T_i was quantitatively described by the equation:

$$E=CT_i-\Delta E_0 \tag{2}$$

For a set of related decomposition processes C is a constant and ΔE_0 represent the zero point activation energy.

To verify the Eq. (2), the E *vs.* T_i data were plotted in Fig. 6.

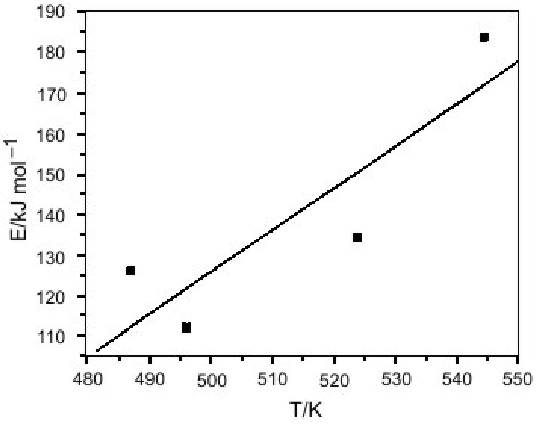


Fig. 6 Linear regression corresponding to Eq. (2)

Parameters of the regression straight line corresponding of Eq. (2) are indicated in Table 5.

Table 5 Parameters of Eq. (2) corresponding to complex decomposition

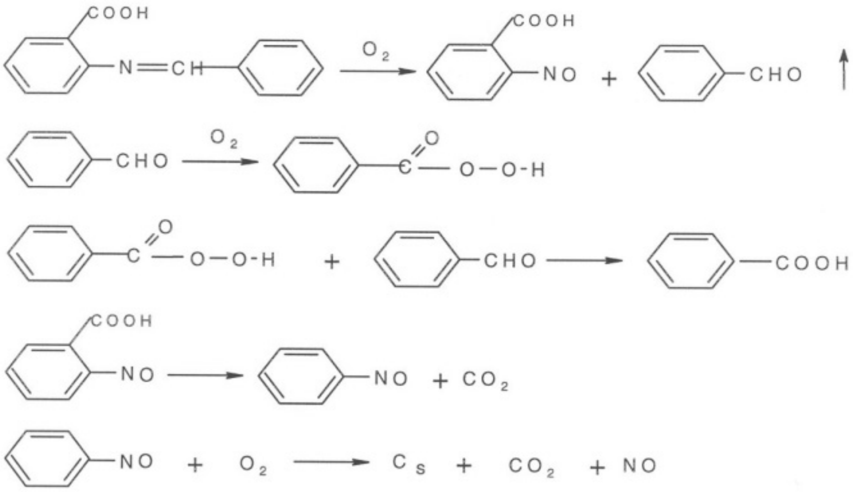
C/kJ mol^{-1} K^{-1}	ΔE_0/kJ mol^{-1}	r
1.018	383	0.8754

C – slope; ΔE_0 – variation of residual zero-point energy; r – correlation coefficient

The poor value of the correlation coefficient may be explained by the fact that the investigated complex present important structural differences and the decomposition process are not really related process.

In a previous paper [9] was shown that the thermal decomposition of pure ligands, begins after melting process, in contrast to the cobalt complex, which decompose in solid state.

Corroborating the IR spectra, TG, DTG and DTA data we proposed for the L_5 the following stages:



Scheme III

Conclusions

1. The initial decomposition temperature of the Co(II) complex is rising in the first stage if in the ligand molecule two aromatic nucleus were introduced.
2. The final thermo-oxidative decomposition temperature are continuous rising by the substitution of methyls' radicals with phenyls' radicals.
3. The electronic attractive effects of the phenyls' radical can explain the smaller stability of Co(L_4) complex comparing with the Co(L_2) complex.
4. The diminution of decomposition temperature, observed for Co(L_4) was explained by the steric impediments and a less compact packing of the molecules in the crystalline network.
5. The kinetic parameters of the thermal decomposition process are considerable modified by the ligands' structural characteristics.
6. Poor linear correlation of energy *vs*. initial decomposition temperature indicates that the decomposition reactions are not a really related process.

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