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Synthesis and Polymerization in Unsaturated Co β-Diketonates

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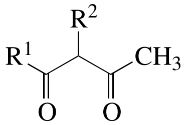
Abstract—Polymerization of some unsaturated β-diketonates of cobalt containing double bonds both unconjugated and conjugated with a metal cycle. Unlike monomeric complexes, cobalt in metal-containing polymers was shown to have tetrahedral structure of the coordination polyhedron. The kinetic parameters of polymerization depend on electronic and steric properties of β-diketonates.

Recently, researchers show great interest in the metal-containing polymers, since they are the promising catalysts and materials with valuable functional properties [1, 2]. One of the most suitable methods for synthesizing metal-containing polymers consists in polymerization of metal-containing unsaturated compounds, in particular, coordination compounds with unsaturated ligands. This method is interesting in that it allows one to produce polymers where all functional groups are bound to the metal ions, i.e., to produce materials with homogeneous chemical composition. However, polymerization of coordination compounds is poorly studied [3–5], although the studies in this field are of unquestionable interest. One of the requirements for the metal complexes as monomers is that they have the high solubility and thermodynamic stability in organic solvents used in the polymerization reactions. With this fact in view, the metal β-diketonates are considered to be suitable models for studying polymerization of coordination compounds.

Previously, we described polymerization of some β-diketonates of Ni(II) [6]. The aim of this work was to synthesize and study polymerization of unsaturated β-diketonates of Co(II) containing both α- and γ-unsaturated substituents.



	R^1	R^2
5-Methyl-5-hexene-2,4-dione (Mhd)	$-C(CH_3)=CH_2$	H
7-Octene-2,4-dione (Od)	$-CH_2-CH_2-CH=CH_2$	H
3-Allylpentane-2,4-dione (Apd)	$-CH_3$	$-CH_2-CH=CH_2$
1,1,1-Trifluoro-3-allylpentane-2,4-dione (Fapd)	$-CF_3$	$-CH_2-CH=CH_2$

EXPERIMENTAL

The β-diketonates used in the synthesis were prepared according to the procedures described in [7, 8]. The cobalt β-diketonate complexes were obtained by reacting an aqueous solution of cobalt acetate (1 mmol) with an alcoholic solution of the corresponding β-diketone (2 mmol). The complexes obtained were filtered off and recrystallized from the alcoholic solutions at room temperature. Since the metal diketonates with unsaturated substituents can polymerize on heating, their purification by vacuum sublimation is undesirable.

The structure and composition of the synthesized compounds were determined from the data of elemental analysis, electronic and IR spectroscopies. The electronic absorption and diffuse reflection spectra were recorded on a Specord M40 spectrophotometer in the range of 25000–11000 cm^{-1}; IR spectra were measured on a Specord M80 spectrophotometer in the range of 4000–400 cm^{-1} (with KBr pellets).

The kinetics of a free-radical polymerization was studied by dilatometric method at 80°C in DMF solution at the monomer concentration 0.15 mol/l and at the concentration of initiator (2,2'-azo-bis(isobutyronitrile)

Table 1. Results of elemental analysis of Co β-diketonates

Complex	Content (found/calcd), %		
	M	C	H
$Co(Mhd)_2 \cdot 2H_2O$	16.93/16.87	48.46/48.38	6.92/6.84
$Co(Od)_2 \cdot 2H_2O$	15.66/15.55	51.24/51.17	7.47/7.38
$Co(Apd)_2 \cdot 2H_2O$	15.66/15.57	51.24/51.15	7.47/7.39
$Co(Fapd)_2 \cdot 2H_2O$	12.16/12.07	39.78/39.7	4.56/4.47

0.0015 mol/l for all complexes. The obtained metal-containing polymers were precipitated from solutions with isopropanol.

RESULTS AND DISCUSSION

The results of elemental analysis of the synthesized β-diketonates of Co indicate the formation of $Co(\beta\text{-Dik})_2 \cdot 2H_2O$ complexes (β-Dik is β-diketone) that are colored red (Table 1). However, these compounds can readily transform into anhydrous blue-colored complexes $Co(\beta\text{-Dik})_2$ or can form as a mixture of two phases.

IR spectra of unsaturated β-diketonates of cobalt are similar to those of metal β-diketonates with bidentately coordinated unsaturated ligand and a delocalized system of π-bonds in a chelate ring (Table 2) [9]. However, these spectra are peculiar in that they contain a band in the region of 1630–1650 cm^{-1} due to the stretching vibration of a double bond ν(C=C) of unsaturated substituents. The bands due to the stretching vibrations ν(Co–O) are slightly shifted toward long-wave region as compared to cobalt acetylacetonate and are close in their parameters to the bands observed for cobalt trifluoroacetylacetonate $Co(Tfa)_2$.

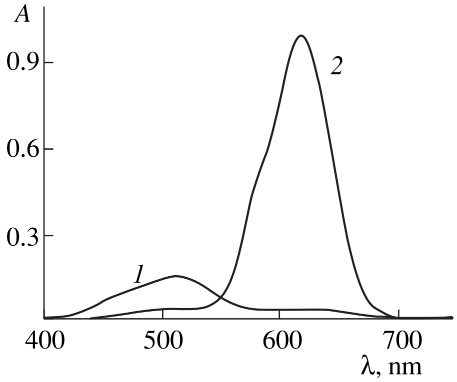
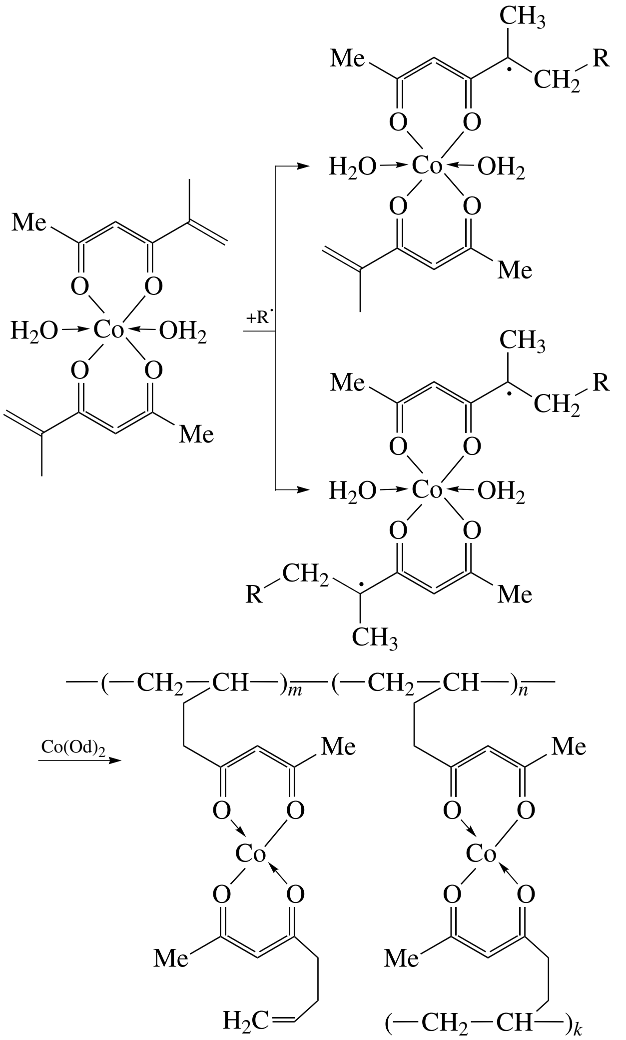


Fig. 1. Electronic absorption spectra of 0.02 M solution of (*1*) monomer and (*2*) 0.002 M solution of polymer of $Co(Mhd)_2$ in DMF.

The electronic absorption and diffuse reflection spectra of the Co complexes are almost identical, which suggests that the complexes in solution and in polycrystalline state have similar structures. The electronic absorption spectra of monomeric complexes contain a broad absorption band at 515 nm that was assigned to the ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition of Co(II) with pseudooctahedral ligand surrounding (Fig. 1, *1*). The coordination sphere of Co is completed to octahedron as the result of coordination of two water molecules. The diffuse reflection spectra of anhydrous complexes indicate the tetrahedral structure of the Co coordination surrounding (the absorption band of Co(II) appears that is characteristic of this symmetry type and corresponds to the ${}^4A_2 \longrightarrow {}^4T_1(P)$ transition at 630 nm).

The radical polymerization of Co β-diketonates can be considered as three parallel reactions (initiation, growth and termination of a chain) that occur at constant rate only at the initial stage of the process:



Shown in Fig. 2 are the kinetic curves of polymerization of 0.15 M solutions of cobalt β-diketonates in DMF. One can see that the polymerization reaction proceeds with a short induction period. The rate of poly-

Table 2. Selected frequencies (cm^{-1}) in IR spectra of monomeric and polymeric Co β-diketonates

Compound	ν(MO)	ν(CO)	ν(CC)	ν(C=C)
$Co(Acac)_2$	450	1598	1598	
$Co(Tfa)_2$	427	1621	1639	
$Co(Mhd)_2$	435	1545	1590	1630
$[Co(Mhd)_2]_n$	<400	1550	1580	
$Co(Od)_2$	435	1560	1580	1645
$[Co(Od)_2]_n$	<400	1555	1575	
$Co(Apd)_2$	435	1550	1590	1630
$[Co(Apd)_2]_n$	<400	1550	1590	1630_{resid}

merization reaction (V_p), the reduced polymerization rate (V_{red}), and the overall rate constant of polymerization (K_Σ) were calculated from the initial sections of polymerizatiaon curves:

$$V_p = \frac{-d[M]}{dt} = \frac{10Ug_m}{M_mV}\frac{1}{t},$$

where [M] is the initial monomer concentration, U is conversion over time t (%), g_m is the weighed portion of a monomer (g), M_m is the molar mass of a monomer, V is the dilatometer volume (ml), t is the polymerization time (s);

$$V_{red} = \frac{V_p}{[M]}$$

and

$$K_\Sigma = \frac{V_p}{[M][I]^{1/2}},$$

where [I] is the starting concentration of initiator. The results obtained are listed in Table 3.

The values of polymerization rate constants suggest that, as in the case with Ni complexes, the reactivity of β-diketonates of Co depends on the nature of β-diketone. The highest polymerization rate at concentration 0.15 mol/l is observed for the Co complex with methacrylacetone $Co(Mhd)_2$. This can be explained by the fact that the given double bond is conjugated with the metal cycle plane. In the case with the fluorinated β-diketonate complex $Co(Fapd)_2$, the polymerization rate and the yield of the metal-containing polymer are substantially lower than in the case of non-fluorinated β-diketonates, which is likely to occur due to delocalization of the electron density on the trifluoromethyl substituent.

It is worth noting that for $Co(Mhd)_2$, the polymerization of complexes in DMF proceeds at the higher rate than in ethanol. The values of V_p for $Co(Mhd)_2$ in DMF are almost one order of magnitude as high as the rates of polymerization of this complex in alcohol ($V_p = 0.87 \times 10^{-3}$ mol/l s) [3]. The authors of [3] failed to obtain metal complexes with the other β-diketones in alcohol solutions. This can be due to the fact that the reaction of polymerization in the alcohol solutions

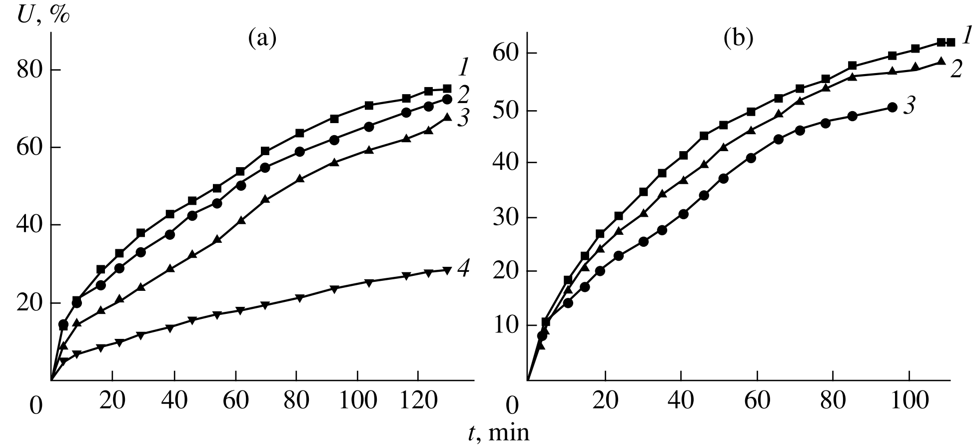


Fig. 2. Kinetic curves of polymerization in DMF of 0.15 M solutions of (a) (*1*) $Co(Mhd)_2$, (*2*) $Co(Od)_2$, (*3*) $Co(Apd)_2$, and (*4*) $Co(Fapd)_2$; (b) (*1*) $Ni(Mhd)_2$, (*2*) $Ni(Od)_2$, and (*3*) $Ni(Apd)_2$ [6].

Table 3. Kinetic parameters of polymerization of 0.15 M solutions of Co β-diketonates in DMF

Complex	$V_p \times 10^5$, mol/(l s)	$V_{red} \times 10^5$, s^{-1}	$K_\Sigma \times 10^4$, $l^{1/2}/(mol^{1/2}\ s)$
$Co(Mhd)_2$	10.33	36.21	13.12
$Co(Apd)_2$	7.45	31.72	10.48
$Co(Od)_2$	10.14	34.78	12.60
$Co(Fapd)_2$	2.93	9.58	3.41
$Ni(Mhd)_2$ [6]	4.28	14.34	7.52
$Ni(Apd)_2$ [6]	3.86	12.96	6.09
$Ni(Od)_2$ [6]	4.88	15.67	7.78

occurs with significant chain transfer to the solvent. Moreover, the system homogeneity can be violated as the result of insolubility of the polymer formed in ethanol.

The isolated metal-containing polymers are finely dispersed powders of blue color. The results of elemental analysis correspond to the calculated composition $[Co(\beta\text{-Dik})_2]_n$, i.e., all the functional groups of a macroligand are bound to the metal ion. IR spectra of polymers exhibit some broadening of the bands due to vibrations ν(CO) and ν(CC) and substantial reduction in the intensity of the bands due to the stretching vibrations of double bonds C=C. The bands corresponding to ν(CoO) are shifted to the region below 400 cm^{-1}, which indicates that this bond becomes weaker after polymerization (Table 2).

The electronic absorption spectra of solutions of poly-β-diketonates of Co in DMF have the shape typical of the Co^{2+} ions with tetrahedral configuration (Fig. 1, *2*). Thus, the composition of the Co^{2+} coordination polyhedron changes during polymerization. It is obvious that the tetrahedral structure of the coordination core is most favorable for macromolecules.

The comparison of the above results with the data that we previously obtained for analogous Ni complexes [6] shows that polymerization of Co^{2+} β-diketonates takes place at the higher rate and with the higher yield (Fig. 2, Table 2) than in the case with Ni^{2+}. This can be explained by the tendency of the Co^{2+} ions to form tetrahedral structures that considerably reduce steric hindrances for the formation of the polymer chains.

It is interesting that in the case with the nickel complexes $Ni(\beta\text{-Dik})_2(H_2O)_2$, the highest polymerization rate was observed for $Ni(Od)_2$ with a flexible α-substituent n-C_4H_7. Obviously, this is due to the fact that in the formation of metal-containing polymers with pseudooctahedral configuration of the chelate unit, the most important role is played by the steric factors rather than the electronic structure: in the given complex, the double bond is located at a significant distance from the metal cycle plane and therefore, the complex polymerization occurs with the least spatial hindrances.

Thus, the results of the above study showed that the reactivity of the metal-containing monomers based on β-diketonates in the polymerization reaction depends on the nature of a metal and β-diketone and is determined both by the electronic and steric factors.

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