SYNTHESIS AND STUDY OF SOME NEW Co(II) POLYPHOSPHINATES
Determination of the kinetic parameters for the thermal decomposition reactions

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Abstract

This paper reports the synthesis and study of some Co(II) coordination polymers with the following acids as ligands: 2,8-dimethylphenoxyphosphinic, diphenyloxyphosphinacetic, diphenylthiophosphinacetic and dihexylphosphinic acids. The study was performed by means of chemical analysis, gel chromatography, IR spectroscopy, ESR, X-ray diffraction, thermogravimetry and electric resistance measurements. The experimental results were used to propose the structural formulae of these compounds and to calculate the kinetic parameters of the thermal decomposition reactions.

Keywords: coordination polymers, semiconductors, thermal behaviour

Introduction

Interest in the coordination polymers with diorganophosphinic acids as ligands dates from 1962, when the first members of the series were synthesized and analysed [1, 2]. Subsequently, many other articles have appeared on their synthesis, thermal properties and potential use as semiconductors or anticorrosion agents [3–12].

Experimental

The synthesis of the above-mentioned coordination compounds were achieved following the testing of different methods and reaction conditions. The best results were obtained from the direct reaction between Co(II) acetylacetonate and 2,8-dimethylphenoxyphosphinic, diphenyloxyphosphinacetic, diphenylthiophosphinacetic and dihexylphosphinic acids, at a molar ratio of 1:2, the reaction mixtures being heated at 165–170°C for 2.5 h. The process was considered completed when the evolved gases, containing acetylacetone, gave a negative reaction with Fe^{3+}. In all cases, the reaction yield was above 99%.

The products were washed with small volumes of water and ethanol, and dried to constant mass at 105°C; blue powders were obtained in all cases. After drying, the
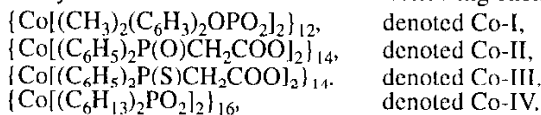
soluble fractions of these compounds were extracted with benzene and afterwards with dimethylformamide. The soluble fractions represented only 2% of the mass of each sample.

The chemical composition was the same for the soluble and insoluble fractions. The results obtained and the molecular mass determined by the cryosopic method in benzene [1, 2] are listed in Table 1.

Table 1 Compositions and molecular mass of the synthesized compounds

Sample	Co%		C%		P%		H%		M
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	
Co-I	10.22	10.81	58.23	58.35	10.74	10.81	4.20	4.31	6980
Co-II	10.22	10.16	58.23	58.40	10.74	10.88	4.20	4.28	8100
Co-III	9.68	9.41	55.17	53.28	10.18	10.25	3.94	3.86	8600
Co-IV	11.80	11.70	54.85	54.91	11.80	11.96	9.90	9.80	8350

Analysis of the above data led to the following chemical formulae:

$\{Co[(CH_3)_2(C_6H_3)_2OPO_2]_2\}_{12}$,   denoted Co-I,
$\{Co[(C_6H_5)_2P(O)CH_2COO]_2\}_{14}$,   denoted Co-II,
$\{Co[(C_6H_5)_2P(S)CH_2COO]_2\}_{14}$.   denoted Co-III.
$\{Co[(C_6H_{13})_2PO_2]_2\}_{16}$,   denoted Co-IV.

The macromolecular dispersions of the synthesized coordination polymers were recorded by means of a Watter apparatus, through gel chromatography on a Stirex column with cyclohexanone as eluent. The working technique was described earlier [4]. All compounds presented only one wide peak (with a shoulder), which corresponded to 40, 35, 30 and 40 ml of eluent for Co I, Co II, CoIII and Co IV, respectively.

Results and discussion

TG and kinetics of the decomposition reactions

The TG analyses were performed with a MOM-Budapest derivatograph, using samples of 100 mg, at a heating rate of 10°C min^{-1}, up to 700°C.

Inspection of the TG curves reveals that the thermal destruction proceeds in two stages with the emission of gaseous products resulting from the organic part of the ligands (Table 2). The final solid products of thermal degradation correspond to the chemical formula of Co(II) metaphosphate. The reaction orders, the activation energies and the preexponential factors were calculated by the Freeman-Carroll [13] and Coats-Redfern [14] methods (Table 3). The two sets of results are in good agreement.

The thermal degradation of the sulphur-containing compound started at a lower temperature than that of the similar compound not containing sulphur. This is due to

Table 2 Characteristic degradation temperatures for some Co(II) polyphosphinates

Sample	Step 1/°C		Step 2/°C		Temperature corresp. to mass loss/°C	
	start	end	start	end	10%	25%
Co-I	340	365	365	605	358	398
Co-II	365	386	386	595	377	421
Co-III	320	341	341	588	335	367
Co-IV	295	320	320	510	310	351

the external electronic structure, which is less stable and more polarizable, and to the marked reducing character of sulphur compared with oxygen.

The reaction orders for the solid-gas systems usually vary between 0 and 1. The fractional values of the reaciton order are due to transport phenomena of the gaseous component through the solid compound, to interphase phenomena or to 'vaporization' of the volatile products. The unhindered chemical reaction would manifest itself at the highest dispersion, the molecular dispersion. Under such conditions, the reaction order would be equal to unity [15] and consequently, the higher the dispersion degree, the higher the reaction order. In our case, the increase in the dispersion degree is achieved as a result of volatile evolution, the reaction order increasing from one stage to another.

IR, ESR and X-ray diffraction spectra

The IR absorption spectra of the studied compounds were recorded by means of a UNICAM spectrometer, in the range of frequencies 400–4000 cm^{-1}. The absorption peaks of the PO_2, PO and PS groups (950–1250 cm^{-1}) [16] and the carboxylic groups (1650–1700 cm^{-1}) were carefully analysed. The spectra obtained were quite similar to those of the corresponding free acids, the differences appearing due to the participation of the above-mentioned groups in the coordinate bonding. The differences resulted in the vibration frequencies lower than for the free acids. This decrease was 2.9% for Co-I and 2.65 for Co-IV. For the polymers Co-II and Co-III, the variation was (3.2±0.1)% and (3.8±0.1)%, respectively, depending on the nature of the analysed group (PO, PS or carboxylic).

The ESR spectra were recorded on solid samples with an RES-IFA București spectrometer. The intensity of the magnetic field was 3216.9 Gauss at a frequency of 9030 MHz, ΔH taking the following values (in Gauss): 24 for Co-I, 25 for Co-II, 38.5 for Co-III and 26 for Co-IV. The g-factor values and the number of uncoupled electrons were computed according to the literature [17]. In all cases, we found that there are three uncoupled electrons corresponding to Co^{2+}.

The diffractograms were recorded on a Kristalloflex-Siemens diffractometer. using CuK$_\alpha$ radiation. All the synthesized compounds presented a two-phase structure: a local characteristic order for the amorphous state and a crystalline state evidenced

Table 3 Kinetic parameters of the decomposition reactions for the synthesized cobalt(II)coordination polymers

Sample	Freeman-Carroll						Coats-Redfern					
	step 1			step 2			step 1			step 2		
	$E_a/$ kJ mol^{-1}	n	$A/$ min^{-1}	$E_a/$ kJ mol^{-1}	n	$A/$ min^{-1}	$E_a/$ kJ mol^{-1}	n	$A/$ min^{-1}	$E_a/$ kJ mol^{-1}	n	$A/$ min^{-1}
Co-I	149	0.68	$4.00 \cdot 10^{13}$	170	0.76	$1.15 \cdot 10^{13}$	143	0.6	$2.95 \cdot 10^{11}$	160	0.8	$2.70 \cdot 10^{11}$
Co-II	196	0.71	$9.88 \cdot 10^{16}$	214	0.79	$7.09 \cdot 10^{15}$	187	0.7	$5.07 \cdot 10^{14}$	200	0.9	$9.96 \cdot 10^{13}$
Co-III	170	0.76	$6.12 \cdot 10^{15}$	188	0.80	$8.27 \cdot 10^{14}$	160	0.8	$3.01 \cdot 10^{13}$	181	0.9	$3.56 \cdot 10^{13}$
Co-IV	125	0.80	$2.50 \cdot 10^{12}$	146	0.85	$7.28 \cdot 10^{11}$	122	0.8	$3.41 \cdot 10^{10}$	139	1.0	$3.30 \cdot 10^{10}$

by some diffraction lines. The degree of crystallinity is quite low, varying from 16% for Co-IV to 31% for Co-II.

Electric conductivity measurements

Coordination polymers containing conjugated double bonds exhibit semiconductor properties. We therefore expected the synthesized polymers, containing phenyl radicals and structural units coordinated at the Co(II) central ion, to display similar properties. With this end in view, we determined the electric conductivities of the samples on pressed pellets in the temperature range 20–200°C and calculated the activation energies by using a method described previously [5].

The experimental data revealed that, in the studied range of temperatures, $\log\sigma$ depends linearly on $1/(4.6kT)$ for the coordination polymers Co-I, Co-II and Co-III. Table 4 lists the σ_{20}, σ_{200} and ΔE values for these compounds. The coordination polymer Co-IV did not present semiconducting properties, possibly because of the absence of π-bonds.

Table 4 Values of the electric conductivity and the activation energy for the synthesized coordination compounds

Polymer	σ_{20}/Ω^{-1} cm^{-1}	σ_{200}/Ω^{-1} cm^{-1}	ΔE/eV
Co-I	$1.6 \cdot 10^{-6}$	$4.7 \cdot 10{-}11$	0.68
Co-II	$2.0 \cdot 10^{-7}$	$5.3 \cdot 10{-}12$	0.98
Co-III	$8.1 \cdot 10^{-8}$	$9.8 \cdot 10{-}12$	1.08

Replacement of the oxygen by sulphur in the ligands (Co-III) resulted in diminished semiconductor properties. This could be due to the differences in electronegativity and polarizability of these two atoms.

Proposed structures of the obtained coordination polymers

The chemical analyses indicated that for every central Co^{2+} there are two corresponding bi- or tridentate anions originating from the organophosphinic acids. Thus, the central ion will be tetracoordinate or hexacoordinate as a function of the ligand; this conclusion is in accord with the IR spectra.

Since the ESR spectra indicate a paramagnetic Co(II) ion having three uncoupled electrons, for tetracoordination an sp^3 hybridization corresponding to the tetrahedral structure is required. When the hexacoordination appears, octahedral structures with an sp^{3}d^2 hybridization of the central ion will be obtained.

The three uncoupled electrons from the outer electron shell of the Co(II) cation will be subjected to the low field created by the ligands. Therefore, according to the crystalline field theory, the seven electrons from the outer electron shell will be disposed on the $e_g^4 t_{2g}^3$ levels for the tetrahedral surrounding, and on the $t_{2g}^5 e_g^2$ levels for the octahedral surrounding [18].
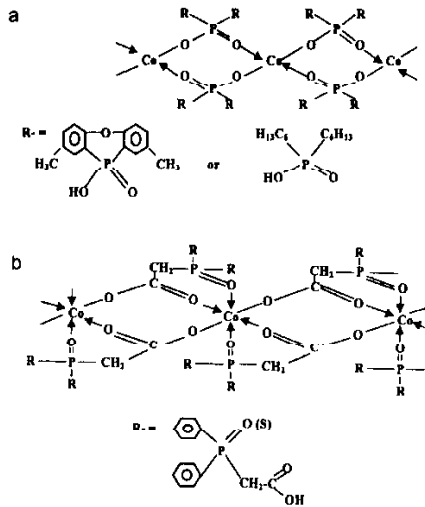
Fig. 1 a – Tetracoordination structure of the Co(II) coordination polymers; b – Hexacoordinate structure of the Co(II) coordination polymers

These arguments lead us to propose the structures presented in Fig. 1 for the synthesized Co(II) coordination polymers.

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