

SHORT COMMUNICATION

Coordination polymers of Fe(III) with ligands derived from dinaphthyl-, dinaphthylthio-, and dinaphthylthiophosphinic acids

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Abstract: The synthesis and the study of some coordination polymers derived from the interaction of the acetylacetonate of Fe(III) with dinaphthylphosphinic acid, dinaphthylthiophosphinic acid and dinaphthylthiophosphinic acid are presented. The methods applied for the study were chemical analysis, gel chromatography, Mössbauer and IR absorption spectroscopy, X-ray diffraction and thermogravimetric analysis from which the kinetic parameters of the thermal decomposition reactions were determined. The semiconductive properties of the synthesized compounds were also examined. Based on the obtained experimental data and on literature indications, the structural formulae of these compounds were assigned.

Keywords: organophosphinic acids, coordinative compounds, Fe(III), Mössbauer, XRD, conductivity.

INTRODUCTION

Continuing the development of the field of coordination polymers based on organophosphinic acids, the synthesis and the study of coordination polymers of Fe(III) with ligands derived from: dinaphthylphosphinic, dinaphthylthiophosphinic and dinaphthylthiophosphinic acids are presented in this paper. The interest for this class of compounds started in 1962, when the first compounds of this type were synthesized and studied.^{1,2} Since then research has continued and a number of important papers have been published.^{3–24} Some of these compounds have high thermal stability,^{3–10} and a small number of them have semi-conductive properties.^{11–13,19–21} Among the latest compounds prepared are those presented in this paper.

RESULTS AND DISCUSSION

The synthesis, chemical analysis, molar weight determination and gel chromatography

The presented compounds were synthesized by different methods under various reaction conditions (in the melt, with or without refluxing in organic solvents). The best results

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were obtained by refluxing a mixture of iron(III) acetylacetonate and one of used phosphinic acids, in a mole ratio of in 1:3 in an organic solvent. The phosphinic acids were dinaphthylphosphinic, dinaphthylthiophosphinic and dinaphthylthiophosphinic. Benzene, toluene and ethanol were used as organic solvents.

A reaction time of three hours was necessary to obtain a 100 % yield. The initial concentration of the reactants was between 0.1–0.3 mol l⁻¹, with benzene used the reflux solvent. When the reaction was completed, the obtained products were separated by evaporation of the solvent. The compounds are washed with distilled water and with ethanol and then dried at a temperature of 105 °C until constant weight. All the compounds are solid brown colored products with a low solubility in organic solvents.

The chemical composition determined by classic methods are presented in Table I, together with molar weights, experimentally determined by ebullioscopy in benzene.^{1–2}

From the chemical analysis and from the mole ratio of the reactants used, the following compounds are obtained: {Fe[O₂P(C₁₀H₇)₂]₃}_n; {Fe[OSP(C₁₀H₇)₂]₃}_n; {Fe[S₂P(C₁₀H₇)₂]₃}_n denoted as Fe – I, Fe – II and Fe – III respectively.

TABLE I. The chemical composition (%) and the molar weight (*M*) of the synthesized compounds

Com- pounds	Fe		C		P		S		H		<i>M</i>
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	
Fe – I	5.56	5.68	71.50	71.75	9.23	9.14	–	–	4.17	4.26	8, 100
Fe – II	5.30	5.45	68.24	68.38	8.81	8.90	9.10	9.2	3.98	4.10	8, 250
Fe – III	5.07	5.16	62.27	62.36	8.43	8.32	17.40	17.51	3.8	3.89	8, 330

Gel chromatography was used for the determination of the degree of dispersion. For this purpose, a Water type apparatus with a column filled with styrex and cyclohexanone as eluent was used. From the registered results, it was observed that the fraction soluble in cyclohexanone gave a single peak. This showed that the analyzed fractions were relatively “homogeneous” in terms of structure and degree of polymerization.

Thermal gravimetric analysis and the determination of the kinetic parameters of the thermal decomposition

Thermal analysis was realized using a Paulik-Erdey instrument using 50 mg samples. A heating rate of 10 °C/min over the temperature range of 20–700 °C was used.

The characteristic temperatures for the thermal decomposition of the studied compounds are presented in Table II. The compounds containing sulfur atoms with an oxidation number of (–2) have a lower decomposition temperature than similar compounds containing oxygen atoms. This fact is due to the reductive character of sulfur atoms. It was also observed that the naphthyl radicals increased the thermal stability of the compounds in which they are present, in comparison to the similar polymers containing alkyl or phenyl radicals.^{10–23}

The activation energy and the reaction order were calculated for every thermal decomposition step, using the Freeman-Carroll method. The results are presented in Table II.

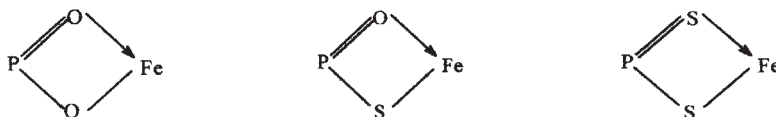
TABLE II. The characteristic temperatures for the decomposition process and the values of the reaction order and activation energy (kJ/mol) of the thermal decomposition reactions of the studied compounds

Compound	Starting temperature °C	End temperature °C	Step I thermal decomposition			Step II thermal decomposition		
			Temp. domain/°C	Reaction order	Activation energy	Temp. domain/°C	Reaction order	Activation energy
Fe – I	425	700	425–485	0.70	241	485–595	0.80	280
Fe – II	365	680	365–420	0.75	230	420–580	0.85	261
Fe – III	355	665	355–415	0.80	221	415–575	0.85	238

The IR absorption spectra

The IR-absorption spectra of the studied compounds were registered in the frequency range 400–4000 cm^{-1} with a SPECORD M82 instrument using the KBr technique.

The registered spectra showed differences only in the range of absorption frequencies characteristic for the groups PO_2 , POS and PS_2 , due to coordination to the central metallic atoms:²⁵



The characteristic absorption bands of the vibration frequencies of the groups PO_2 , POS and PS_2 are modified because of the elongation of the PO and, respectively, the PS bonds. Hence these groups in the synthesized compounds absorb at lower values than the corresponding groups in the free acids.

The characteristic absorption frequencies for the $\text{P}=\text{O}$ groups from dinaphthylphosphinic acid lie between 1160–1190 cm^{-1} and for the $\text{P}=\text{S}$ group from dinaphthylthiophosphinic acid and dinaphthylidithiophosphinic acid, between 718–750 cm^{-1} and 800–845 cm^{-1} , respectively.

The IR absorption bands of the groups: $\begin{array}{c} \diagup \\ \text{P}=\text{O} \\ \diagdown \\ \text{OH} \end{array}$ are between 2800–2900 cm^{-1} ; 2525–2725 cm^{-1} ; 2080–2380 cm^{-1} ; 1139–1191 cm^{-1} ; 1600–1740 cm^{-1} ; 917–1040 cm^{-1} and 450–540 cm^{-1} . The absorption bands in the field 1450–1435 cm^{-1} and 1005–995 cm^{-1} , resulting from the $\text{P}-\text{C}_{\text{benzene ring}}$ bond are narrow and of moderate intensity.

The values of the vibration frequencies of the $\text{P}=\text{O}$ and $\text{P}=\text{S}$ groups are modified by coordination of Fe^{3+} and differ by 2.3, 3.2 and 3.8 percent for compounds Fe-I, Fe-II and Fe-III, respectively.

The higher displacement of the group $\text{P}=\text{S}$ is due to the electronic structure of sulfur atoms, which is easier distorted than that of oxygen. Also, sulfur is more polarizable than oxygen which also results in a stronger coordinative bond formation.

The Mössbauer spectroscopy

The Mössbauer spectra of the studied compounds were registered with an electrody-

namics installation with uniform accelerated movement of the source. The ^{57}Co isotope in a chromium matrix was used as the source. The values for the isomer displacements were measured using sodium nitroprusside as the standard sample. The determinations were made at room temperature (300 K) and also at liquid nitrogen temperature (80 K).

The characteristic parameters determined from Mössbauer spectroscopy are: isomer displacement (chemical); temperature displacement, quadrupole splitting and hyperfine magnetic splitting.

The thermal spectral displacement represents approximately 0.05 mm/s 100 °C. The decrease of the δ value (Table III) is a consequence of the decreasing ionic character of iron-(III) in the synthesized compounds.

The derived compounds do not show quadrupole splitting because of the spherical symmetric electronic configuration ($3d^5$) of the central Fe(III) atom.

TABLE III. The values of the parameters of the Mössbauer spectra of the studied compounds

Compound	T/K	$\delta/(\text{mm/s})$	$\Delta E_Q/(\text{mm/s})$	$\Gamma/(\text{mm/s})$
Fe – I	300	0.56	0.71	0.63
	80	0.83	0.76	0.50
Fe – II	300	0.54	0.03	0.70
	80	0.64	0.20	0.50
Fe – III	300	0.58	0.84	0.46
	80	0.76	0.64	0.80

Studying the Mössbauer spectra leads to the conclusion that in all the studied complexes, the iron is in the (+III) oxidation state with high value of the spin number ($S = 5/2$) which indicates a weak character of the Fe-ligand bond. Comparing the values of the isomer displacement δ , a resemblance of "s-type" electronic density around the nucleus is observed. A small difference appears for the quadrupole splitting, easy observable for the Fe-II compound when the central atom iron(III) is octahedrally surrounded by three atoms of oxygen and three atoms of sulfur, derived from the dinaphthylthiophosphinic acid anion. In this compound a decrease of the symmetry of the environment of the central atom is observed with an electronic distribution nonequivalent on the molecular orbitals in the rectangular axes directions. The central iron(III) atom has the highest symmetry in compounds Fe-I and Fe-III when all the six atoms that surround the iron(III) atom are oxygen atoms (for Fe-III compounds).

The values of the ΔE_Q parameter show that the central atom iron(III) is octahedrally coordinated in all the studied compounds.

It should also be noticed that the values of Γ increase with decreasing temperature which can be explained by a relaxation effect. For all the studied compounds, a temperature dependence of the isomer displacement was observed, presenting higher values than usual for Fe(III), which is in accordance with a Doppler effect of the second degree. It is probable that on increasing the temperature from 80 to 300 K, an increase of the oscillation of the Fe(III) atom in the crystalline lattice occurs. Also, a displacement of the "s" type electronic density along the ligand-central atom bond is observed.

Comparing the values of the isomer displacement δ for all the studied compounds, a similarity of the "s" electronic distribution can be seen from the Mössbauer spectral parameters

X-ray diffraction

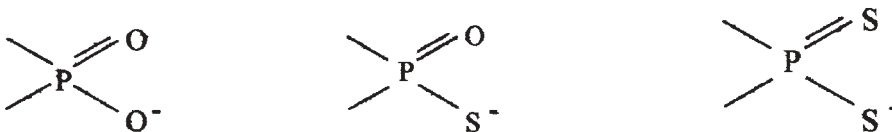
The characterization of the studied compounds by X-ray diffraction was accomplished by computing the diffractogrammes of solid samples registered using a Kristalloflex Siemens apparatus with $\text{Cu}(\text{K}\alpha)$ radiation filtered through Ni at an anodic potential of 35 kV and a current of 12 mA. The diffraction domain covered by this apparatus is $2\theta = 10 - 45^\circ$.

The X-ray diffractogrammes confirm the fact that all the synthesized compounds have a two phases structure with amorphous and crystalline zones.

From the X-ray diffractogrammes, the values for the degree of crystallinity were computed. Values of 25.6 %; 18.9 % and 15.3 % were found for Fe-I, Fe-II and Fe-III, respectively.

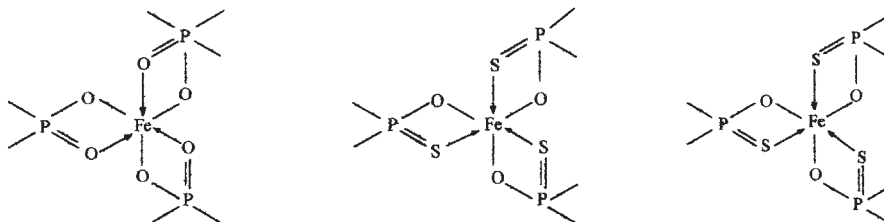
The structure of the studied compounds

An octahedral structure of the polymers was assigned from the combination rate of Fe(III) with the anions of the acids used as bidentate ligands with the oxygen and sulfur atoms from the groups:



This structure was confirmed by chemical analysis, by the absorption bands of the groups present in the synthesized compounds shown previously, in comparison with the spectra of the free acids.

Also, the Mössbauer spectra categorically show that the central iron(III) atoms are hexa-coordinated in octahedral structures of the type:



It was experimentally proven that the structure of coordination polymers of Cr(III) with anions derived from diphenylphosphinic acid corresponded to a spiral arrangement of octahedral units containing as a center the hexacoordinated metallic cation.²

Based the experimental data presented here and on other mentioned references, the

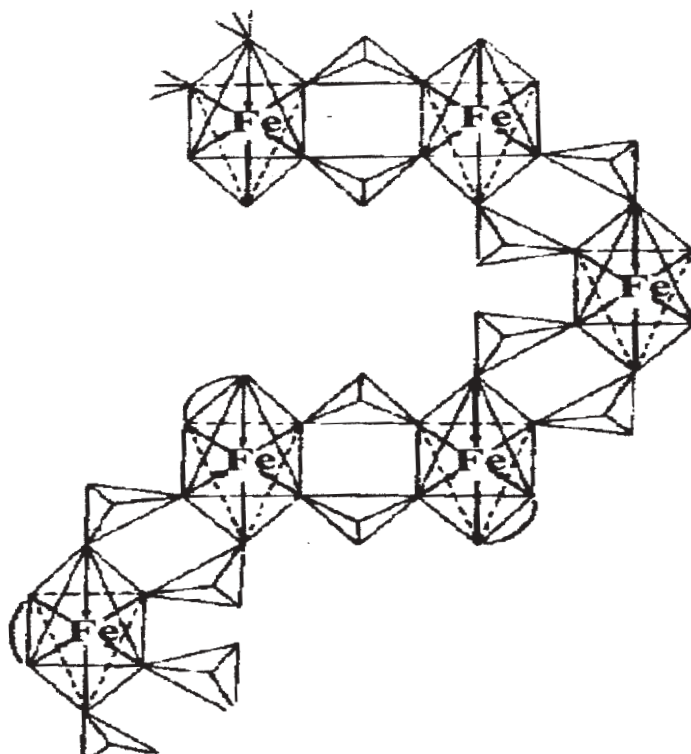


Fig. 1. The octahedral structure disposal in the studied coordination polymer chains.

octahedral structures of the studied polymers was confirmed, similar to other coordination polymers with ligands of the same type presented previously.²

Determination of the electrical conductivity and of the activation energy

The electrical conductivity was determined for the temperature domain 20 to 200 °C on solid samples of 12 cm diameter obtained under a pressure of 10 tone/cm². The measurements were made using a Tesla 283 Megaohm-meter with aluminum electrodes of 1 cm² transversal section. The measurements were made first at 200 °C, then the sample were cooled to 20 °C and the measurements repeated. The values of the activation energy were computed¹³ and are presented in Table IV.

TABLE IV. The values of the electrical conductivity (ohm⁻¹ cm⁻¹) and of the activation energy (kJ mol⁻¹) for the studied compounds at the temperatures of 50, 100, 150 and 200 °C

Compound	κ_{50}	κ_{100}	κ_{150}	κ_{200}	E
Fe – I	9.4×10^{-11}	5.32×10^{-10}	2×10^{-9}	5.69×10^{-9}	0.72
Fe – II	3.9×10^{-11}	2.56×10^{-10}	9.64×10^{-10}	2.74×10^{-9}	0.82
Fe – III	1.8×10^{-11}	1.61×10^{-10}	6.05×10^{-10}	1.76×10^{-9}	0.91

CONCLUSIONS

The compounds studied in this paper were obtained by refluxing the reactants iron(III) acetylacetonate with one of the ligands: dinaphthylphosphinic, dinaphthylthio-phosphinic and dinaphthylthiophosphinic acids, in an organic solvent (benzene, toluene, etc.). The mole ratio of the reactants was in all cases 1:3.

The values of the molar weights of the compounds determined in benzene showed that they are oligonic (average degree of polymerization is 8). The ligands are bidentate. Hexa-coordinated octahedral structures are formed. This fact was confirmed by Mössbauer spectroscopy. These structures are similar to other coordination polymers of the same type presented in other papers.¹⁻¹⁷

The practical importance of these compounds results from their semi-conductive properties and high thermal stability, properties that are very rarely exhibited in the same compound.

ИЗВОД

КООРДИНАЦИОНИ ПОЛИМЕРИ Fe(III) СА ЛИГАНДИМА ИЗВЕДЕНИМ ОД ДИНАФТИЛ-, ДИНАФТИЛТИО- И ДИНАФТИЛДИТИОФОСФИНСКЕ КИСЕЛИНЕ

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Приказане су синтезе и резултати проучавања неких координационих полимера који настају интеракцијом ацетилацетоната Fe(III) и динафтилофосфинске киселине, динафтилтиофосфинске киселине или динафтилдитиофосфинске киселине. При томе су коришћене: хемијска анализа, гел хроматографија, Мосбауер и IR апсорпциона спектроскопија, рендгенска дифракција, као и термогравиметријска анализа, за одређивање кинетичких параметара реакција термичког разлагања. Такође, одређиване су и полупроводничке особине синтетизованих једињења. На основу добијених резултата и литературних података овим једињењима су приписане и одговарајуће структурне формуле.

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