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THE SYNTHESIS AND THE STUDY OF THE COORDINATION POLYMERS OBTAINED BY THE INTERACTION BETWEEN Pd(II) ACETYLACETONATE WITH DIPHENYLPHOSPHINIC, DIPHENYLTHIOPHOSPHINIC AND DIPHENYLDITHIOPHOSPHINIC ACIDS AS LIGANDS

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ABSTRACT. The synthesis and the study of some coordination polymers derived from the interaction of acetylacetonate of Rh(II) with diphenyl-phosphinic acid, dipheylthiophosphinic acid and diphenyldithiophosphinic acid are presented. The methods applied for the study are: chemical analysis, IR-absorption spectra, ESR, Spectroscopy, X-ray diffraction, the registration of some curves on a derivatograph and the determination of the kinetics parameters of the thermal decomposition reactions. Based on experimental data and on literature indications, the structural formulas of these compounds are assigned.

INTRODUCTION

From the synthesis of the first compound derived from the class of polymers obtained by the interaction between acetylacetonate of metals with organophosphinic acids (poly-[diμ-diphenylphosphinato-acetylacetonate Cr(III)] obtained in 1962 [1] till present days a lot of compounds were synthesized and studied. The obtained compounds presented similar structures and some important practical properties (semiconductors, birefrigence anticorrosive protection, high thermal stability, a.s.o.) [2-9]. Almost all the synthesized compounds are coordinated polymers.

In this work, a continuation of the authors research in this field is presented. The paper consists in the synthesis and the study of the obtained coordination polymers by the interaction of Pd(II) acetylacetonate with the following acids: diphenylphosphinic, diphenylthiophosphinic and diphenyldithiophosphinic.

The IR-absorption spectra, ESR and X-ray diffraction spectra were recorded and also the derivatographic curves in order to determine the kinetics parameters of the thermal decomposition were registred. The molecular weight was determined and the dispersion curves were registred by a gel-cromatograph.

RESULTS AND DISCUSSIONS

a) The synthesis, the elemental analysis, molecular weight and dispersion degree. The synthesis of the studied compounds occurred by different methods and conditions but the best results obtained through the direct reaction between Pd(II) acetylacetonate and one of the acids: diphenylphosphinic, diphenylthiophosphinic and diphenyldithiophosphinic at a molar rate of 1 : 2, by heating for two hours and a half, at a temperature of 170^{0}C. The heating process lasted until in the resulted gas-compounds (containing acetylacetone) the characteristic reaction for acetylacetone with the ferric ion is not observed. When the reaction was over, the final compounds were wasched with distilled water and then dried at the temperature of 150^{0}C at constant weight. After drying, the soluble fractions from these compounds were separated by solving them in ethanol and then in benzene. The solubility of these compounds in ethanol varied between 2-3% and in benzene between 3-5%. The most soluble compound was the polymer derived from Pd(II) acetylacetonate with diphenyldithio-phosphinic acid.

The determined chemical composition obtained by classic methods applied to the soluble and insoluble samples in the mentioned solvents is presented in Table 1. It is shown that the experimental values are almost equal to those determined by calculations. Together with the values of the chemical composition, the molecular weight determined by cryoscopic methods applied in benzene are also presented in Table 1.

Table 1.

Elemental composition (%) and molecular weight for the synthesized

The compounds derived from:	Pd^{2+}	C	P	O	H	M
	calc. exp.	calc. exp.	calc. exp.	calc. exp.	calc. exp.	
$Pd(Acac)_2$ + $2(C_6H_5)_2PO_2H$	19.69 19.80	53.29 53.50	11.47 11.65	11.84 11.92	3.70 3.82	3800
$Pd(Acac)_2$ + $2(C_6H_5)_2POSH$	18.58 18.75	50.31 50.40	10.82 10.95	5.59 5.72	3.49 3.54	5200
$Pd(Acac)_2$ + $2(C_6H_5)_2PS_2H$	17.60 17.69	47.65 47.74	10.25 10.53	- -	3.30 3.41	5.500

We considered useful to apply this method for determining the molecular weight, because some other researchers (for example, Black [1] and others [2-9]) applied it for the same type of coordination polymers, so it is interesting for comparison reasons.

All the synthesized compounds are brown solids.

From the chemical analysis and from the ratio of the reactants, it is shown that chemical reactions occur as following:

$$n\,Pd(Acac)_2 + 2n(C_6H_5)_2PO_2H \rightarrow \{Pd[(C_6H_5)_2PO_2]_2\}_n + 2n\,HAcac$$
$$n\,Pd(Acac)_2 + 2n(C_6H_5)_2POSH \rightarrow \{Pd[(C_6H_5)_2POS]_2\}_n + 2n\,HAcac$$
$$n\,Pd(Acac)_2 + 2n(C_6H_5)_2PS_2H \rightarrow \{Pd[(C_6H_5)_2PS_2]_2\}_n + 2n\,HAcac$$

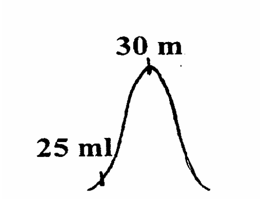


Fig. 1. The registred gel-cromatography curve for Pd-I using styrex and ciclohexanone as eluent

For an easier writing of the formulas, the following notations are used: $\{Pd[(C_6H_5)_2PO_2]_2\}_n$ is noted Pd-I, $\{Pd[(C_6H_5)_2POS]_2\}_n$ is noted Pd-II, $\{Pd[(C_6H_5)_2PS_2]_2\}_n$ is noted Pd-III.

For all the synthesized compounds the dispersion degree was determined using the gel-cromatographic method. The instrument used was a Watter type cromatograph with a column filled with styrex, using as solvent ciclohexanone.

From the registered curves it is shown that all the compounds presented a single peak not very sharp (Fig.1). As sharper the peak is as omogenous the polymer is concerning the polymerization degree and the structure. The volume of eluent (ml) where the peak appears is conversely proportional with molecular weight of the respective polymer.

b) Thermal-gravimetric-analysis and the establishing of the kinetics parameters of the thermal decomposition. For the thermal-gravimetric analysis, a derivatograph Paulik-Erdey was used; the samples used had 50 mg weight, at a heating speed of 10^0C/min and the temperature was between 20^0C and 700^0C.

Studying the registred curves obtained by derivatographic method of the synthesized compounds, it can be observed that the thermal destruction occurs in phases, by releasing gaseous products derived from the organic parts of the used acids. The final solid compounds resulting from the reaction correspond as chemical composition to Pd(II) metaphosphat.

The thermal destruction occurs in two stages for all the synthesized compounds and starts at a temperature of about 300^0C (Table 2). The reaction order and the activation energy corresponding to the thermal decomposition stages are determined using the Freeman and Carol method [10] (Table 2).

Table 2.

The two stages of the thermal decomposition, the values of the reaction order and of the activation energy [kj/mol]

The compound	Stage 1 (^{0}C)		Stage 2 (^{0}C)		Reaction order		Activation energy	
	Start	End	Start	End	Stage 1	Stage 2	Stage 1	Stage 2
Pd-I	295	390	390	560	0.83	0.88	150	175
Pd-II	285	375	375	570	0.80	0.85	135	158
Pd-III	280	370	370	570	0.80	0.85	130	150

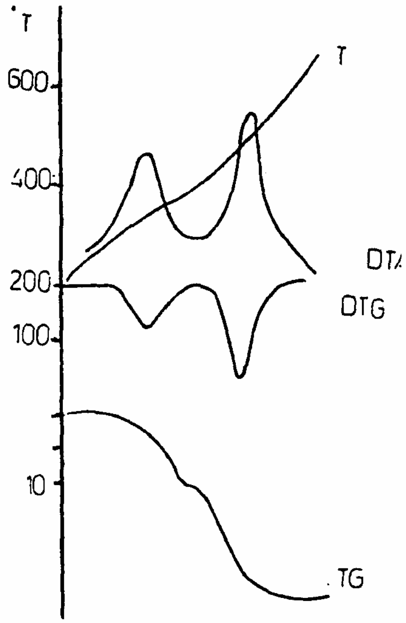
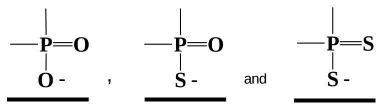


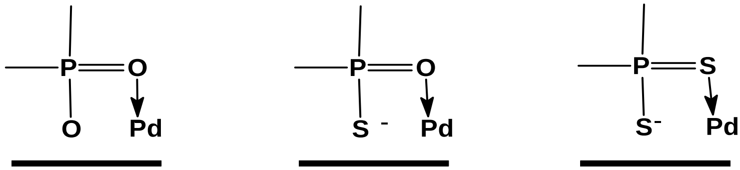
Fig. 2. The derivatographic curves of Pd-I.

From the experimental data it is shown that the beginning of the thermal decomposition for the synthesized compounds occurs at lower temperatures for the S-containing compounds than fot the similar ones without S-atoms (Table 2). This fact is justified by the exterior electronic structures of the S-atoms that is less stable more polarizable and with a greater reducing character of sulphur in comparison with the structure of O-atoms from the groups from the synthesized compounds.



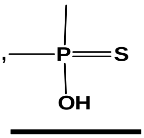
c) The IR-Absorption Spectra. The IR-absorption spectra of the studied compounds were registred using an instrument "Unicam" with a frequency band of 400-4000 cm^{-1}. Primarly, it was studied the absorption in the field of frequncy 950-1250 cm^{-1} that is characteristic for the groups PO_2 and PS_2.

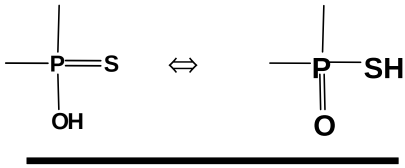
Generally, the IR-absorption spectra of the synthesized compounds are similar with those of the free acids. The differences arise only in the field of absorption of the groups $>PO_2^-$, $>POS^-$ and PS_2^- due to the coordinaton to the central atom Pd(II):



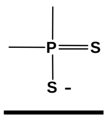
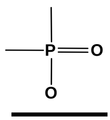
For the group P=O, the characteristic absorption spectra, $\nu_{P=0}$ is between the values 1261 cm^{-1} and 1087 cm^{-1}, for the molecules that contain hydroxilic (-OH) groups bound to the phosphorous atom [11,12].

For the acid $(C_6H_5)_2PO_2H$, were observed a diffuse band in the 3000-3100 cm^{-1} range and two usual bands in the 2200-2360 cm^{-1} and 909-932 cm^{-1} ranges.

For the compounds that contain the group,  the following tautometric equilibria is observed:



The substitutes presenting an electronic deficiency decrease the basicity of the group P=O and are favorable to the formation of the thiolic-isomer. The group P=S is less basic than the group P=O and that is why the equilibrium is favorable to the formation of the thio-isomer in benzene and chlor-benzene media. In aqueous or alcoholic solutions, the equilibrium is favorable to the thio-isomer.

For the coordinated groups and  to  the central atom Pd(II), the frequencies of the absorption vibrations $\nu_{P=O}$, $\nu_{P=S}$ for the free acids and for the coordination compounds derived from the same acids, differences noted $\Delta\nu$, the following equation is established:

$$\Delta\nu = \frac{\nu - \nu'}{\nu} \cdot 100$$

This equation represents the percent modifications of the vibration frequencies of the same group (P=O or P=S) from free acids towards the synthesized compounds.

The values corresponding to the synthesized coordination compounds Pd-I, Pd-II, Pd-III are 3.1, 3.9, 4.5. These values show a stronger bound of the P=S groups in the coordination compounds in comparison with the P=O groups.

d) The ESR-Spectroscopy. The ESR-spectra were registred for the solid samples with a spectrometer RES-IFA Bucharest.

Studying the ESR-spectra it was shown that the central atom Pd(II) had one of the two possible electronic structures $4d^8$:

↑↓	↑↓	↑↓	↑↓		or	↑↓	↑↓	↑↓	↑	↑

From the experimental data it is noted that all the synthesized compounds presented in this paper have a diamagnetic stucture, which means that the exterior electronic structure is formed by pairs of electrons in orbitals: 4d, 5s and 5p; the central atom Pd(II) has a planar structure as it is observed in almost all complex combinations of this metal [13-15].

e) The X-ray Diffraction Spectra. The X-ray diffraction spectra for the synthesized compounds were registred using a Kristalloflex-Siemens instrument that has a Roentgen tube with Cu(K) radiations filtred through Ni. The anode voltage is 35 kV and the intensity is 12 mA. The irradiation technique consists in transmission using the continuous exploration of the diffraction spectra with Geiger-Müller counter situated on a texture goniometer. The diffraction field was of $2\theta = 10\text{-}45^0$. From the X-ray diffraction spectra the crystallinity degree was established using the equation:

$$X_C = \frac{F_C}{F_C + F_A} \cdot 100 ,$$

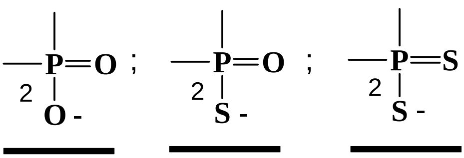
where: F_C represents the crystalline halo area and F_A - the amorphous halo area.

All the synthesized compounds have a bi-phase structure: one characteristic for the amorphous state and the second with diffraction lines characteristic for the crystalline phase. The crystallinity degree for the synthesized compounds is relatively small having the values: 23% for Pd-I; 16% for Pd-II and 12% for Pd-III.

CONCLUSIONS

The proposed structure for the synthesized compounds

From the chemical analysis it is shown that for every central atom of Pd(II) correspond two anions of: diphenylphosphinic, diphenylthiophosphinic or diphenyl-dithiophosphinic acids. These data mean that the central atom Pd(II) is surroundet with four oxygen atoms or four sulphur atoms or two oxygen and two sulphur atoms or two oxygen and two sulphur atoms derived from the two anions of the respective acids:



From the IR-absorption spectra it was deduced that the groups

$>PO_2^-$, $>POS^-$ and $>PS_2^-$, from the acids are bidentate coordinated.

Every central atom is bounded with two acid anions and tetracoordinated structures of Pd(II), result which can be tetrahedron or planar. Because of ESR-spectroscopy shows that all the synthesized compounds are diamagnetic, the conclusion is that the dsp^2 hybridization is established and the planar configuration of Pd(II) as central atom results.

From the experimental data it is shown that all the synthesized compounds are polymers having the molecular weights, for the benzene soluble fractions, between the limits 3800-5500, that correspond to a polymerization degree of 7 and 9, respectively.

Based on the mentioned facts, it results that the structures of the synthesized coordination compounds are those of a polymer derived from the concatenation of the planar structures of the central atom Pd(II) (Fig.3). This resulted structure is similar to literature indications [14,15] concerning the planar structures of almost all tetracoordinated compounds of Pd(II).

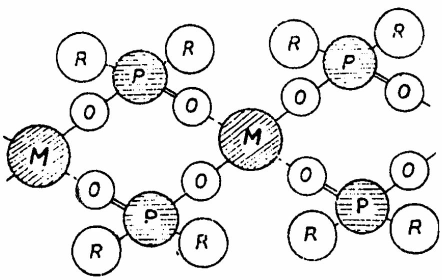


Fig. 3. The structure assigned for the synthesized compounds

REFERENCES

1. P.B. Block, J. Simkin, R.L. Ocone, *J.Am. Chem. Soc.*, 1962, ***84***, 1749.
2. A. Stone, G.A.W. Graham, *Inorganic Polymers*, Acad. Press, London, 1962.
3. V.V. Korsak, P.C. Krukovski, *Viskomolek Soed.*, 1967, ***A69***, 583.
4. T. Golotiu, I. Roşca, *Makromolek. Chem.*, 1972, ***160***, 59.
5. I. Roşca, *Viskomolek. Soed.*, 1985, ***B1***, 34.
6. I. Roşca, *Viskomolek. Soed.*, 1985, ***B10***, 735.
7. C. Silvestru, I. Haiduc, *J. Organomet. Chem.*, 1989, ***365***, 83.

8. C. Silvestru, I. Haiduc, F. Caruso, M. Rossi, B. Mahieu, M. Gielen, *J. Organomet.Chem.*, 1993, ***448***, 75.

9. I. Roşca, D. Sutiman, A. Cailean, M. Vizitiu, I. Rusu, D. Sibiescu, *Thermochim. Acta.*, 1995, ***269/270***, 295.

10. S.E. Freeman, B. Carol, *J. Phys. Chem.*, 1958, ***62***, 394.

11. I. Kossler, *Methoden der Infrarot Spectroscopie in der chemischen Analyse*, Akad. Verlog., Leipzig, 1961.

12. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc. New York, London, 1963.

13. A. Okaya, *Paramagnetic Resonance*, Akad. Press, New York, 1963.

14. 0J. Lewis, R.G. Wilkinson, *Modern Coordination Chemistry*, London, New York, 1988.

15. M. Brezeanu, P. Spacu, *Chimia combinațiilor complexe*, Ed. Did. Pedag., Bucharest, 1986.