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Studies regarding the thermal stability of some coordination polymers. Polydiphenylphosphinates and polydialkylphosphinates of Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and UO_2^{2+} ☆

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Abstract

In order to obtain coordination polymers resistant at high temperatures, many compounds from a new class of coordination polymers, having as ligands anions of diphenylphosphinic acid and dialkylphosphinic acid, have been prepared and studied; this started in 1962.

In this paper, we report our continuing studies, recording and discussing TG curves obtained using a MOM Budapest derivatograph. The effect of oxygen from air versus temperature on the above-mentioned coordination polymers was examined. The temperatures that corresponded to the beginning and end of the thermal decomposition and also the temperatures at which 10% and 25% of the samples are transformed to volatile compounds were used to estimate the thermal stability. The kinetic parameters of the thermal decomposition were also computed.

These studies were made using samples of coordination polymers with the general formula $[M(R_2PE_2)_x]_n$, where, M is Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and UO_2^{2+}, R is C_2H_5, C_4H_9 and C_6H_5 radicals, E is oxygen or sulphur, x is 2 or 3, and n is the polymerization degree.

Discussing the experimental data we conclude that the thermal stability is higher: in nitrogen atmosphere; for polymers that contain the phenyl radicals and Mn(II); and for the same cation in the series: polyphosphinate > polythiophosphinate > polydithiophosphinate.

The reaction order and the activation energy calculated using the Freeman–Carroll method presented values between 0.75 and 0.95 and 125 and 464 kJ mol^{-1} respectively.

Keywords: Coordination polymer; Dialkylphosphinate; Diphenylphosphinate; Stability; TGA

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1. Introduction

One of the most successful ways of obtaining chemical compounds consists of using many cations and organic ligands in order to synthesize coordination compounds, particularly coordination polymers with special properties that make them more applicable in some fields than organic compounds.

In the past, the main direction in polymer chemistry was the field of organic compounds. Today inorganic macromolecular compounds and coordination polymers are more often studied. The present paper studies the thermal stability of the polydiphenylphosphinates and polydialkylphosphinates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and UO_2^{2+}. From the first synthesis of this class of coordination polymers, using as ligands derivates of diorganophosphinic acid and acetyl-acetone (poly-[di-μ-phenylphosphinato-acetyl-acetonato chromium(III)], obtained in 1962 [1]) until now, many other compounds of this class, which maintain their properties (birefringence, semiconductors, adhesives, anticorrosive, etc.) at high temperatures, have been synthesized and studied [2–4].

The present paper is a continuation of our studies regarding the synthesis and thermal stability of these coordination polymers, with discussion of the recorded derivatographic curves and the determination of their kinetic parameters of thermal decomposition [5–9]. The coordination polymers were obtained by the interaction of acetylacetonates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and UO_2^{2+} with diphenylphosphinic acid, diphenylthiophosphinic acid, diphenyl-dithiophosphinic acid, dibutylphosphinic acid, diethylphosphinic acid, diethylthiophosphinic acid and diethyldithiophosphinic acid.

2. Experimental

2.1. Reagents and equipment

For the synthesis of the above-mentioned coordination compounds, the following acids were used: diphenylphosphinic acid $HPO_2(C_6H_5)_2$ [10]; diphenylthiophosphinic acid $HPSO(C_6H_5)_2$ [11]; diphenyldithiophosphinic acid $HPS_2(C_6H_5)_2$ [12]; dibutylphosphinic acid $HPO_2(C_4H_9)_2$ [13]; diethylphosphinic acid $HPO_2(C_2H_5)_2$ [14]; diethylthiophosphinic acid $HPSO(C_2H_5)_2$ [15]; and diethyldithiophosphinic acid $HPS_2(C_2H_5)_2$ [16].

The acetyl-acetonates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and UO_2^{2+} used in the synthesis were obtained by methods indicated in literature: acetyl-acetonate of chromium(III), $CrAcac_3$ [17]; acetyl-acetonate of manganese(II), $MnAcac_2$ [18]; acetyl-acetonate of iron(III), $FeAcac_3$ [19]; acetyl-acetonate of cobalt(II), $CoAcac_2$ [20]; acetyl-acetonate of nickel(II), $NiAcac_2$ [21]; and acetyl-acetonate of uranyl, UO_2Acac_2 [22].

The following high-purity organic solvents were used: benzene, toluene, ethanol, acetone, chloroform and butanol.

The experiments were carried out using the following equipment: a Knokh-Bloc instrument for elemental analysis; a cryoscopic instrument for molecular weight determination; an atomic absorption spectrometer for metallic cation determinations. AAS1-Carl Zeiss Jena; a derivatograph MOM-1500Q for the thermal stability determination, samples of 50 mg were used at a heating rate of 10°C min^{-1}; a spectrometer RES-IFA Bucuresti, for electronic spin spectra determinations; and a Kristalloflex-Siemens diffractometer with CuKα radiation to evaluate the amorphous and crystalline zones.

2.2. *Methods and techniques*

The synthesis of the coordination polymers presented in this paper was carried out by polycoordination in melted mixtures and by refluxing in one of the following solvents: benzene, toluene, ethanol, butanol, acetone or chloroform.

Stoichiometric amounts (0.3:0.1 or 0.2:0.1 moles) of diorganophosphinic acid and acetyl-acetonate of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) or uranyl were introduced into a 500 ml flask and then heated a little over the melting point of the acid, if the polycoordination process was carried out by melting methods. If the synthesis was carried out by refluxing in organic solvents, the stoichiometric amounts of the reagents were placed together with 500 ml of solvent in a 1000 ml flask equipped with an Allihn condenser. In both cases, the reaction was considered to be completed if after 3–4 h, no further acetyl-acetone was obtained.

For compounds obtained by the melting method, the amount of product dissolving in benzene, toluene, acetone, ethanol, butanol and chloroform, was only slight (maximum 1–2 g in 100 ml solvent).

If the polycoordination process was carried out by refluxing the solvent, a small amount of the obtained product remained dissolved in the solvents used.

When the polycoordination process was finished, the solid compound was separated by filtration, washed several times with ethanol, and finally dried at 105°C, to constant weight.

In all cases, the reaction yield was very close to 100%.

The fraction of the product soluble in benzene was analysed elementally and the molecular weight was determined by a cryoscopic method. This method was also used by other authors for the same coordination polymers [1–4].

The same fraction, soluble in benzene, was subjected to a thermal decomposition and analysed with a derivatograph, and also the ESR and X-ray spectra were recorded.

3. Results and discussions

3.1. *The chemical composition and the molecular weight*

The chemical composition was established by the elemental analysis and the molecular weight was determined with a cryoscopic method. The data are presented in Table 1.

Table 1
The composition and the molecular weights of the synthesized coordination polymers

Polymer	C%		P%		S%		M%		Experimental molecular weight
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	2	3	4	5	6	7	8	9	10
Cr-II	58.38	59.80	10.60	10.20	10.33	10.90	8.42	8.10	8700
Cr-III	53.50	54.50	9.52	9.80	19.68	20.20	7.98	8.40	9800
Cr-IV	46.80	46.10	12.21	12.00	–	–	11.27	11.80	7600
Cr-V	39.61	40.10	15.71	15.50	–	–	13.18	12.60	5700
Cr-VI	36.62	37.20	14.51	14.30	15.01	14.30	12.31	13.50	5700
Cr-VIII	33.32	33.80	13.51	13.20	23.91	23.30	11.33	12.30	7400
Mn-I	54.80	53.30	12.68	12.30	–	–	11.28	11.80	3980
Mn-II	57.18	55.80	11.90	11.70	12.30	12.80	10.50	10.10	5290
Mn-III	52.06	52.60	11.20	11.10	23.20	23.90	9.93	9.40	7790
Mn-IV	46.91	47.50	15.11	15.30	–	–	13.44	13.80	6420
Mn-V	32.30	32.90	20.83	20.40	–	–	18.70	18.20	1850
Mn-VI	29.21	29.60	18.80	18.50	19.41	19.10	16.70	16.10	3150
Mn-VII	26.79	26.10	17.15	17.00	35.48	35.20	15.21	15.80	3670
Fe-I	59.00	58.30	10.50	10.40	–	–	9.48	9.20	8880
Fe-II	58.30	59.30	9.98	9.60	10.28	10.60	9.90	9.50	7750
Fe-III	33.20	33.80	9.47	9.20	19.57	19.10	8.54	8.80	11000
Fe-IV	46.48	45.30	12.15	12.50	–	–	10.92	11.20	7990
Fe-V	39.21	39.70	15.55	15.30	–	–	14.02	14.30	4400
Fe-VI	36.31	36.80	14.40	14.20	14.84	14.10	13.00	13.40	5050
Fe-VII	33.30	33.50	13.40	13.10	27.80	26.50	12.11	12.60	7890
Co-II	54.86	54.20	11.80	11.30	12.20	11.40	11.20	10.50	6100
Co-III	51.70	53.20	11.10	11.00	23.00	23.10	10.60	10.70	6200
Co-IV	46.50	46.80	15.00	15.60	–	–	14.20	14.80	7400
Co-V	31.90	29.80	20.60	18.90	–	–	19.60	18.60	2700
Co-VI	28.80	27.80	18.60	17.50	19.20	17.80	17.70	16.80	3400
Co-VII	26.30	25.70	17.00	15.20	35.00	32.60	16.10	15.50	6100
Ni-II	54.80	53.80	11.80	11.80	12.20	11.90	11.20	10.60	8600
Ni-III	51.70	52.10	11.10	11.10	23.00	23.50	10.60	10.90	6600
Ni-IV	46.50	47.20	15.00	15.10	–	–	14.20	14.80	5200
Ni-V	31.90	30.50	20.60	19.70	–	–	19.60	19.10	4800
Ni-VI	28.80	27.90	18.60	18.10	19.20	18.50	17.70	17.10	5800
Ni-VII	26.30	25.80	17.00	16.50	35.00	34.80	16.10	15.80	7100
UO_2^{2+}-I	40.90	39.30	8.80	9.20	–	–	33.80	39.50	4300
UO_2^{2+}-II	39.10	38.30	8.40	8.10	8.70	8.10	32.30	33.50	5200
UO_2^{2+}-III	37.50	38.10	8.00	8.30	16.60	17.10	31.00	31.60	3400
UO_2^{2+}-IV	30.70	31.00	9.90	10.10	–	–	38.10	38.40	5100
UO_2^{2+}-V	18.70	17.80	12.10	12.50	–	–	46.50	46.10	5800
UO_2^{2+}-VI	17.60	16.80	11.40	10.80	11.70	11.30	43.70	44.30	5900
UO_2^{2+}-VII	16.60	17.30	10.70	11.30	22.20	22.40	41.30	41.80	5300

Studying the chemical composition of the synthesized compounds, it is shown that for every Cr^{3+} or Fe^{3+} cation, there are three anions of the respective acids, and for Mn^{2+}, Co^{2+}, Ni^{2+} and UO_2^{2+}, only two anions of the respective acids.

The established formulae for the synthesized compounds are:

$\{M[PO_2(C_6H_5)_2]_x\}_n$, denoted as Fe-I, Mn-I, Co-I, Ni-I, UO_2^{2+}-I;
$\{M[POS(C_6H_5)_2]_x\}_n$, denoted as Cr-II, Mn-II, Fe-II, Co-II, Ni-II, UO_2^{2+}-II;
$\{M[PS_2(C_6H_5)_2]_x\}_n$, denoted as Cr-III, Mn-III, Fe-III, Co-III, Ni-III, UO_2^{2+}-III;
$\{M[PO_2(C_4H_9)_2]_x\}_n$, denoted as Cr-IV, Mn-IV, Fe-IV, Co-IV, Ni-IV, UO_2^{2+}-IV;
$\{M[PO_2(C_2H_5)_2]_x\}_n$, denoted as Cr-V, Mn-V, Fe-V, Co-V, Ni-V, UO_2^{2+}-V;
$\{M[POS(C_2H_5)_2]_x\}_n$, denoted as Cr-VI, Mn-VI, Fe-VI, Co-VI, Ni-VI, UO_2^{2+}-VI;
$\{M[PS_2(C_2H_5)_2]_x\}_n$, denoted as Cr-VII, Mn-VII, Fe-VII, Co-VII, Ni-VII, UO_2^{2+}-VII.

From the molecular weight values, established cryoscopically, the media polymerization degree of the synthesized compounds is between 10 and 16; for a few compounds the polymerization degree is less than 10 or higher than 20.

3.2. *The thermal stability and the kinetics of the decomposition reactions*

Studying the registered curves, it was observed that the polymer fractions that are soluble in organic solvents melted, and then the thermal decomposition process, in almost all cases, took place in two very distinct stages. The fractions that are insoluble in organic solvents decomposed without melting (Fig. 1).

For the polymers containing sulphur, the thermal stability was higher in an inert atmosphere than in the presence of oxygen from the air. This behaviour is due to the fact that the sulphur atoms, because of their reducing character, in the presence of oxygen and because of the temperature, are oxidized to sulphur dioxide. All polymers containing sulphur, heated in normal atmosphere, were transformed into compounds in which sulphur is replaced with oxygen. This is related to the chemical analysis which is in accordance with the registered diagrams and corresponds to the reaction taking place at temperatures higher than 200°C for almost all polymers

$$\{M[PS_2(C_6H_5)_2]_x\}_n + 3nO_2 \xrightarrow{^\circ C} \{M[PO_2(C_6H_5)_2]_x\}_n + 2n\,SO_2$$

The final solid products of the thermal decomposition of the polymers correspond to the formulae of the respective metal phosphates or to metallic oxide and pentoxide of phosphorus in different ratios.

For the polymers containing oxygen, the thermal decomposition temperature is a little higher in an inert atmosphere than in air.

Polymers containing Mn(II) have a higher thermal stability; the decomposition temperature is over 300°C or even 500°C. The compound Mn-I has the highest thermal stability and the starting temperature of the decomposition process is 510°C.

The polymers containing ethyl or butyl radicals and sulphur atoms have lower thermal stabilities.

Although there are many ways to characterize the thermal stability, we have chosen the following parameters: the starting and final temperatures of the thermal destruc-

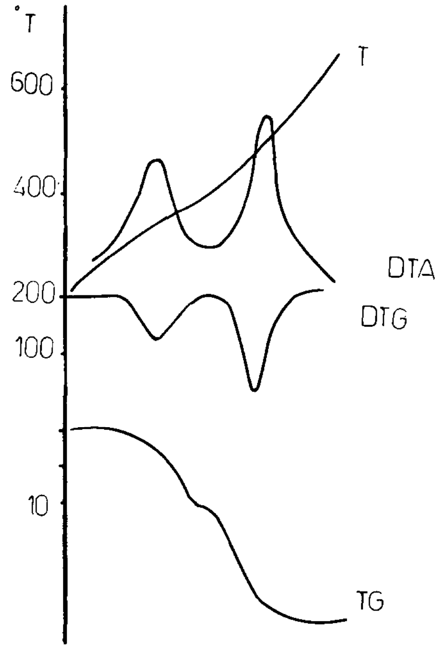

Fig. 1. TG, DTG and DTA curves for the coordination polymer Cr-III.

tion, and the temperature corresponding to 10% and 25% weight losses. These data are presented in Tables 2–7.

The values of the reaction order and activation energy were calculated using the Freeman–Carroll method [23].

Table 2
Characteristic temperatures, and values for the reaction order and the activation energy of the thermal decomposition of the synthesized coordination polymers of chromium(III)

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
Cr-II	300	660	410	440	300–420	420–660	0.80	0.95	167.2	242.4
Cr-III	250	650	400	435	250–415	415–650	0.90	0.95	158.8	234.0
Cr-IV	220	560	310	405	220–350	350–500	0.85	0.90	125.4	209.0
Cr-V	220	510	300	320	220–325	325–560	0.90	0.95	150.5	225.7
Cr-VI	210	420	280	310	210–315	315–420	0.80	0.90	137.9	217.3
Cr-VII	200	415	260	305	200–310	310–415	0.90	0.95	158.8	230.0

Table 3
Characteristic temperatures, and values for the reaction order and activation energy of the thermal decomposition of the synthesized coordination polymers of manganese(II)

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
Mn-I	510	720	575	700	510–720	–	0.90	–	463.1	–
Mn-II	383	700	540	690	385–460	460–700	0.90	0.95	386.2	413.8
Mn-III	320	695	520	680	320–440	440–695	0.85	0.95	374.5	404.2
Mn-IV	230	620	355	470	230–340	–	0.80	–	432.2	–
Mn-V	360	560	400	440	360–560	–	0.95	–	300.9	–
Mn-VI	250	545	325	385	250–390	390–545	0.88	0.95	161.3	284.2
Mn-VII	210	535	285	370	210–380	380–545	0.90	0.95	146.3	200.6

Table 4
Characteristic temperatures, and values for the reaction order and activation energy of the thermal decomposition of the synthesized coordination polymers of iron(III)

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
Fe-I	420	700	495	610	420–700	–	0.75	–	263.3	–
Fe-II	365	680	448	615	365–510	510–680	0.75	0.90	188.1	309.3
Fe-III	350	660	475	598	350–490	490–660	0.85	0.95	171.4	292.6
Fe-IV	264	700	300	375	264–330	330–700	0.80	0.85	137.9	284.2
Fe-V	240	660	380	410	240–320	320–660	0.85	0.90	158.8	300.9
Fe-VI	210	633	300	495	210–300	300–610	0.80	0.85	150.5	275.8
Fe-VII	198	610	360	450	198–310	310–630	0.80	0.88	142.1	246.6

Because in almost all cases only two stages are distinguished in the destruction process, two values for the reaction order and for the activation energy were computed.

The reaction orders had values smaller than unity and the values for the activation energy were between 125.4 and 463.1 kJ mol^{-1}.

The fractional values of the reaction order are due to transport phenomena of the gaseous compounds through the solid, to interphase phenomena and also to "vaporization" of the volatile compound.

Table 5
Characteristic temperatures, and values for the reaction order and activation energy of the thermal decomposition of the synthesized coordination polymers of cobalt(III)

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
Co-II	265	550	305	365	255–350	350–550	0.90	0.95	167.2	292.6
Co-III	250	545	310	355	250–350	350–545	0.90	0.95	154.6	284.2
Co-IV	265	520	315	360	230–375	375–480	0.85	0.90	136.3	239.0
Co-V	285	515	310	400	285–390	390–520	0.90	0.95	146.3	259.0
Co-VI	195	520	295	350	195–320	320–555	0.95	0.95	125.4	246.6
Co-VII	185	520	290	340	185–340	340–540	0.90	0.95	133.7	255.0

Table 6
Characteristic temperatures, and values for the reaction order and activation energy of the thermal decomposition of the synthesized coordination polymers of nickel(II)

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
Ni-II	280	610	350	430	280–595	–	0.83	–	146.3	–
Ni-III	275	600	340	420	275–385	385–600	0.85	0.90	158.8	221.5
Ni-IV	220	450	280	310	220–360	360–450	0.90	0.95	147.2	230.0
Ni-V	230	430	270	300	230–350	350–430	0.85	0.90	146.3	209.0
Ni-VI	210	420	250	290	210–340	340–420	0.90	0.95	134.0	238.3
Ni-VII	200	420	240	280	200–300	330–425	0.80	0.85	126.0	232.0

The unhindered reaction can only take place at the highest dispersion value, the molecular dispersion. Under these conditions, the reaction order would be equal to 1. The higher the dispersion degree, the higher the reaction order, the maximum value being 1. For the thermal decomposition that takes place in two stages, the growing dispersion degree is due to chemical reaction after elimination of the volatile compound. We conclude that for the first stage of the thermal decomposition the value of the reaction order is lower than the values that correspond to the subsequent stages.

Table 7
Characteristic temperatures, and values for the reaction order and activation energy of the thermal decomposition of the synthesized coordination polymers of uranyl

Polymer	Thermal decomposition/°C		Temperature corresp. to weight loss/°C		Field of temperature for calculating the reaction order and activation energy		Reaction order		Activation energy/kJ mol^{-1}	
	Start	Final	10%	25%	1	2	n_1	n_2	E_1	E_2
UO_2^{2+}-I	395	522	460	495	395–520	–	0.85	–	305.0	–
UO_2^{2+}-II	295	523	370	430	295–350	350–525	0.80	0.85	167.0	296.8
UO_2^{2+}-III	280	525	330	480	280–330	330–625	0.80	0.90	150.0	288.4
UO_2^{2+}-IV	300	700	420	520	300–380	380–700	0.85	0.90	180.0	267.5
UO_2^{2+}-V	260	540	380	465	260–390	390–540	0.90	1.00	188.0	275.8
UO_2^{2+}-VI	205	530	295	405	205–370	370–495	0.85	0.90	159.0	259.0
UO_2^{2+}-VII	190	535	242	355	190–360	360–535	0.80	0.90	167.0	276.0

Studying the registered diagrams for the synthesized coordination polymers we can conclude the following:

(i) The thermal stability of almost all these compounds increases in the following order for the metallic element enclosed: Co(II) < Ni(II) < UO_2^{2+} < Cr(III) < Fe (III) < Mn (II);

(ii) The stability of the compounds containing sulphur in the structure of the organic ligand is lower than that of the compounds containing oxygen atoms;

(iii) For the series of polymers containing the same central metallic ion, the highest stability is presented by the polymer with phenyl radicals and the lowest stability is established for the polymers with ethyl radicals;

(iv) The polymers containing sulphur atoms heated in oxygen atmosphere transform into oxygenated compounds by replacing the sulphur atoms with oxygen, and after that they are decomposed in the same way as the oxygenated compounds from the same series of coordination polymers;

(v) The thermal stability of the coordination polymers is much higher than that of the organic ligands used which indicates, that groups susceptible to thermal effects become stronger through polymerization because of the formation of more stable chelate rings.

3.3. *ESR and X-ray diffraction spectra*

Studying the ESR spectra for the synthesized compounds and taking account of the literature values [24], the "*g*"-factor values and the number of uncoupled electrons established for the metallic central ion were computed. Diphenylpicrylhydrazine and nitroso-potassium disulphonate were used as standard substances.

There are three uncoupled electrons for every central atom for all compounds containing Cr(III) ions, and one uncoupled electron for those compounds that contain Mn(II), Fe(III) and Co(II) as central metallic atoms. The other compounds that contain Ni(II) and UO_2^{2+} are diamagnetic, so that all the electrons are coupled.

The "*g*"-factor values for all the studied compounds are higher than those established for the uncoupled electron for all the polymers containing Mn(II), Fe(III) and Co(II).

The paramagnetic and diamagnetic properties of all studied compounds can be explained knowing the electronic exterior structures in the fundamental state for all central atoms: Cr^{3+} $3d^3$, 3 uncoupled electrons; Mn^{2+} $3d^5$, 5 uncoupled electrons; Fe^{3+} $3d^5$, 5 uncoupled electrons; Co^{2+} $3d^7$, 3 uncoupled electrons; Ni^{2+} $3d^8$, 2 uncoupled electrons; U^{6+} $6s^26p^6$, all electrons coupled.

The paramagnetic properties are due to one uncoupled electron for every central atom for all polymers containing Mn(II), Fe(III), Co(II), and to the three uncoupled electrons for the polymers containing Cr(III); the diamagnetic properties are related to the pairs of coupled electrons for all the polymers containing Ni(II) and UO_2^{2+}.

As a result of the interaction of the ligand field (because of the sulphur and oxygen atoms) with the central metallic ions we conclude that:

(i) For the polymers containing Mn^{2+} and Fe^{3+}, four of the five uncoupled electrons become coupled, and for the compounds containing Co^{2+}, two from the three uncoupled electrons become coupled; for these compounds there is only one remaining uncoupled electron for each central atom;
(ii) For the polymers containing Cr^{3+}, all three uncoupled electrons remain uncoupled because of the highest stability of the 3d-level occupied by 3 electrons in three orbitals ($3d^3$);
(iii) For the polymers containing Ni^{2+} as central ion, both uncoupled electrons become coupled because of the ligand field interaction with the central metallic ion.
(iv) For the polymers containing U^{6+} as central atom, because of the exterior electronic structure with all the electrons coupled, this structure remains unmodified after the coordination of the respective ligands.

These experimental data are of great importance for establishing the spatial configuration of the coordination polymers and will be the subject of a future paper.

Studying the X-ray spectra for the coordination polymers containing Cr(III), Fe(III), UO_2^{2+} and of the polymers Ni-II, Ni-III, Co-II and Co-III, a characteristic local order for the amorphous state is established.

For the polymers Mn-IV, Mn-V, Mn-VI, Mn-VII, Co-IV, Co-V, Co-VI, Co-VII, Ni-IV, Ni-V, Ni-VI and Ni-VII, the crystallinity degree varies between 8.8% and 53.2%, which indicates, for these compounds, a two-phase character presenting a local characteristic order for the amorphous state and also diffraction lines that characterize the crystalline state.

The polymers presenting crystalline zones are formed by Mn(II), Co(II) and Ni(II) as central atoms with a small volume and also some small organic ligands which have a smaller number of carbon atoms in the structure of the radicals (ethyl and butyl radicals).

Table 8
Crystallinity degree of the synthesized coordination polymers (X_C)

Polymer	X_C%	Polymer	X_C%	Polymer	X_C%
Co-IV	22.8	Ni-IV	48.8	Mn-IV	22.7
Co-V	27.9	Ni-V	53.2	Mn-V	28.4
Co-VI	23.9	Ni-VI	45.6	Mn-VI	15.0
Co-VII	21.2	Ni-VII	39.8	Mn-VII	8.8

For the polymers containing Cr(III), Fe(III), UO_2^{2+}, and some of those containing Mn(II), Co(II) and Ni(II), probably because of the higher volume of phenyl radicals, only a local order characteristic for the amorphous state is obtained, see Table 8.

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