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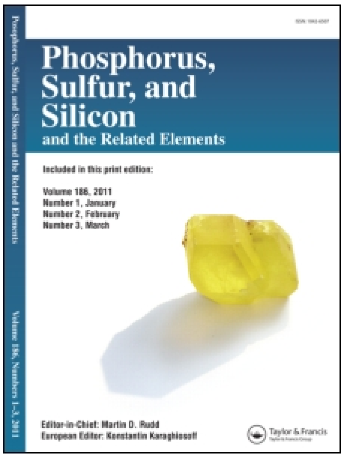

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Structural Considerations on Some Inorganic Polymers of Fe(III) with Phosphorus Containing Rings

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The compounds were synthesised by the reactions between Fe(III) acetylacetonate with each of the following acids: diphenylphosphinic, diphenyltiophosphinic and diphenylditiophosphinic, diethylphosphinic, diethyltiophosphinic, diethylditiophosphinic. The studies were performed by means of Mössbauer, IR and ESR spectroscopy and X-ray diffraction.

Keywords: ionic character; octahedral symmetry; crystallinity; thermal stability

1. INTRODUCTION

An interesting group of compounds containing inorganic rigs are the coordination polymers, their properties being strongly influenced by their structure[1, 2]. Our research has focused on the coordination polymers of Fe(III) because the Mössbauer spectroscopy can bring supplementary information on their structure, information that could be useful even for other series of polymers.

2. EXPERIMENTAL

The studied compounds were obtained according to literature [2] and have the following formulas and abbreviations:

$Fe_2Acac_4[PO_2(C_6H_5)_2]_2$ denoted as Fe-I
$\{FeAcac[PO_2(C_6H_5)_2]_2\}_n$ denoted as Fe-II
$\{Fe[PO_2(C_6H_5)_2]_3\}_n$ denoted as Fe-III
$\{Fe[POS(C_6H_5)_2]_3\}_n$ denoted as Fe-IV
$\{Fe[PS_2(C_6H_5)_2]_3\}_n$ denoted as Fe-V
$\{Fe[PO_2(C_2H_5)_2]_3\}_n$ denoted as Fe-VI
$\{Fe[POS(C_2H_5)_2]_3\}_n$ denoted as Fe-VII
$\{Fe[PS_2(C_2H_5)_2]_3\}_n$ denoted as Fe-VIII

The Mössbauer spectra were recorded by means of electrodynamic type equipment with a uniform accelerate movement of the source, at room temperature and at 80K. As source, we have used the ^{57}Co isotope in chromium matrix. The IR analyses were performed on Specord M80 equipment, in the frequency range 400-4000 cm^{-1}. The ESR spectra were recorded on an IFA spectrometer and the X-ray analyses were performed on a Kristalloflex-Siemens diffractometer.

3. RESULTS AND DISCUSSION

Applying the Mössbauer spectroscopy we have determined the values of the four characteristic parameters (i.e. isomeric displacement - δ, temperature displacement, quadrupol scission - ΔE_Q and hyperfine magnetic scission - Γ). The obtained results are listed in Table 1. From the values ΔE_Q, one can draw the conclusion that the central Fe(III) atom has an octahedral surrounding in all the studied compounds and the symmetry depends on the nature of atoms bound to the central atom. Six atoms of oxygen, coming from the bidentate diphenylphosphinic and diethylphosphinic anions, surround the central ions from Fe-III and Fe-VI. For the polymers Fe-V and Fe-VIII the central atom's surrounding is realised by six sulphur atoms coming from the diphenylphosphinic and diethylphosphinic anions. In this two cases we got the highest octahedral symmetry. The Fe-IV and Fe-VII compounds have a lower symmetry because different atoms (three of oxygen and three of sulphur) surround the central atoms. Despite the fact that their central atoms are octahedrally surrounded, the Fe-I and Fe-II polymers don't have a very high symmetry because their ligands are different (acetylacetone and diphenylphosphinic acid). The compounds with a low symmetry have a nonequivalent electronic distribution on the molecular orbitals vs. the rectangular axes. The experimental data have shown that in all polymers the Fe(III) ions have high spin (S = 5/2), indicating a weak covalent character of the Fe-ligand bond. The comparison of δ values indicate a similarity among all the compounds for the s type electronic density around the nucleus. Among the studied compounds we have ascertained a larger temperature dependence of the isomeric displacement, comparing with the usual ones, which is in agreement with the second degree Doppler effect. We suppose that as a matter of temperature increasing from 80 to 300, concomitantly with the increase of iron ions vibrations, also occurs a displacement of the s type electronic density from the ligand to metal bond. We also noticed that the lower the temperatures the higher the Γ values, fact which can be explained by the relaxation effect. The displacement of the Mössbauer line is linearly dependent on temperature.

Compound	T (K)	δ	ΔE_Q	Γ
Fe-I	80	0.77	0.59	0.79
	300	0.68	0.88	0.33; 0.43
Fe-II	80	0.56	0.52	0.70
	300	0.48	0.60	0.03; 0.84
Fe-III	80	0.63	0.77	0.67
	300	0.41	0.76	0.59
Fe-IV	80	0.85	0.76	0.50
	300	0.54	0.71	0.52; 0.63
Fe-V	80	0.65	0.54	0.65
	300	0.44	0.66	0.80
Fe-VI	80	0.85	0.76	0.50
	300	0.54	0.71	0.52
Fe-VII	80	0.80	0.28	0.48
	300	0.50	0.15	0.1; 0.70
Fe-VIII	80	0.76	0.64	0.80
	300	0.58	0.84	0.46

TABLE 1. Values of the Mössbauer spectra parameters (mm/s)

The changes of the IR frequency values for the P=O and P=S groups after complexation indicate that the P=S group frequency is more affected that of the P=O group. Therefore, the acids containing sulphur atoms are better complexing agents than those containing only oxygen are. According to the ESR data all the compounds are paramagnetic with five impair electrons. The X-ray diffraction data show that all the compounds have a biphasic character (crystalline and amorphous). The quite large percent of amorphous phase suggests a molecular structure that is difficult to order into a crystal cell.

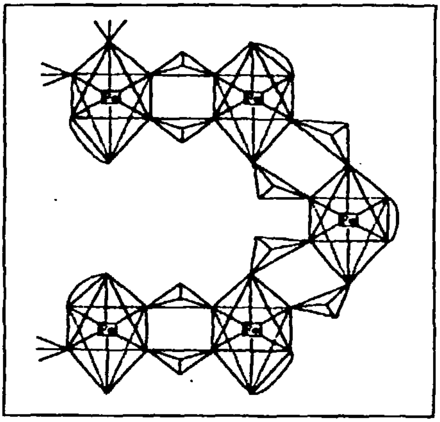

FIGURE 1. The proposed structure for the Fe(III) coordination polymers with diorganophosphinic acids

4. CONCLUSIONS

The experimental data suggest, in good agreement with previous conclusions, a polymeric structure with Fe(III) octahedrons bounded in trans position by means of the tetrahedral structures of the phosphorus atoms, that come from the organophosphinic acids (Figure 1) [3].

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