Manganese (II) modified heteropoly compounds studied by ESR

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Tungstophosphoric lacunary heteropoly compounds modified with manganese ions ($[PW_{11}Mn_x]^{5-}$, $x = 1 - 0.02$) were studied by means of ESR spectroscopy in the range of X-band. Presence of two manganese (II) species of different symmetry, characterized by two signals, one with $g =\sim 2$ and the second with $g = 4.3$, were found.

KEY WORDS: lacunary HPW; ESR; UV–vis; manganese (II).

1. Introduction

High catalytic activity of heteropoly compounds (HPC) for many different reactions has attracted attention since many years. HPC of Keggin structure are the best known and easily synthesized polyoxometalates. The modification of the Keggin structure by means of the replacement of tungsten or molybdenum terminal atoms by transition metal cations (TPC) results in the formation of systems, which can be considered as inorganic metalloporphyrin analogues [1]. Hill and coworkers [2,3] have demonstrated the catalytic activity of lacunary heteropoly compounds of the Keggin structure modified with transition metal ions such as Mn (II), Fe (III), Cr (III) and Co (II).

Several ESR studies on environmental symmetry of transition metal ions located in octahedral lacuna of lacunary Keggin unit and also their susceptibility for oxidation process have been carried out [4,5]. Pope and coworkers [4] have found that the oxidative susceptibility of manganese (II) ions introduced into octahedral lacuna was influenced by central atom (P, Si, B, Zn) present in the Keggin structure. They reported that Mn (II) ions located in $PW_{11}O_{39}$ structure, contrary to $SiW_{11}MnO_{39}$, $ZnW_{11}MnO_{39}$ and $BW_{11}MnO_{39}$, cannot easily be oxidized to higher valences. Noticeable activity of manganese-modified lacunary heteropoly compounds for oxidation of hydrocarbons performed in a liquid phase was reported [2,3]. Lyon *et al.* [6] have shown that $PW_{11}O_{39}$ modified by Mn(II) and Cr (III) cations oxidized propane in a batch reactor under oxygen pressure at a relatively low temperature (100–175 °C). We have also found [7,8] that manganese-modified lacunary $HPW_{11}Mn$ showed high activity for oxidative dehydrogenation of light paraffins in a continuous flow reactor at 400 °C. The oxidative activity was influenced significantly by the manganese cations concentration. Samples containing stoichiometric amount of Mn (II) ions (Mn(II) : KU = 1 : 1) showed rather low activity, which grew with the increase of manganese ions concentration. Manganese cations introduced into lacunary HPW may occupy either an octahedral position in the lacuna or they can be located in a cationic position. The parameters of the ESR spectra may deliver information about the location and the environment of manganese ions in the $Na(Cs)PW_{11}MnO_{39}$ system.

2. Experimental

Sodium salt of lacunary HPW ($Na_7PW_{11}O_{39}$) was synthesized according to [9,10]. To introduce manganese cations into octahedral lacuna of heteropoly anion, aqueous solution of sodium salt ($NaPW_{11}$) was treated with an appropriate amount of $MnCl_2$ under reflux (Mn : KU molar ratio = 1, 0.2, 0.1 and 0.02). Manganese-modified samples of $Na_5PW_{11}Mn_{(x=0.02-1)}O_{39}$ were precipitated with alcohol or they were got from the solution by water evaporation at 70 °C. The samples were dried at 80 °C and stored in a desiccator. Correctness of synthesis was confirmed by FT-IR and Raman spectra.

Cesium salts of lacunary heteropoly acid modified with manganese ions were precipitated by the addition of appropriate amount of Cs_2CO_3 into an aqueous solution of $Na_5PW_{12-x}Mn_xO_{39}$ ($x = 1 - 0.02$).

ESR spectra of lacunary heteropoly compounds modified with Mn (II) ions were recorded at room temperature using ESR spectrometers working in the X-band.

3. Results and discussion

Correctness of the structure of lacunary heteropoly compound $NaPW_{11}O_{39}$ and manganese-modified sam-

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ples $NaPW_{11}Mn_xO_{39}$ synthesized according to [9,10] was confirmed by FT-IR (figure 1) and Raman (figure 2) spectra. The FT-IR spectra presented in figure 1 showed splitting of v_3PO_4 band of value equal $49\,cm^{-1}$ for nonsubstituted lacunary $NaPW_{11}$ and $27\,cm^{-1}$ for the manganese-modified one. These values of Δv splitting for nonsubstituted and manganese-substituted lacunary HPW were very near to those that were found by Rocchiccioli-Deltcheff and Thouvenot [11,12] and also by Hill *et al.* [10] for lacunary HPW. The quoted authors have found that the lacunary nonsubstituted heteropoly compound of $NaPW_{11}O_{39}$ showed the Δv splitting of v_3PO_4 equal to about $45\,cm^{-1}$, while the transition metals introduced into octahedral lacuna resulted in different values of Δv, which varied in the following range: Cu (40) > Zn (38) > **Mn (27)** > Fe (24) > Co (20) > Ni (0). The comparison of IR bands presented in figure 1 with the results described by Rocchiccioli-Deltcheff and Thouvenot [11,12] showed clearly that manganese ions were introduced into octahedral lacuna. Nevertheless, part of manganese (II) cations occupies the cationic positions, which are discussed below on the grounds of ESR spectra.

Some additional arguments about the presence of Mn(II) in the Keggin structure were delivered from the comparison of Raman spectra recorded for the regular Keggin structure ($H_3PW_{12}O_{40}$), lacunary sodium salt ($N_7PW_{11}O_{39}$) and manganese (II) modified lacunary HPW ($Na_5PW_{11}MnO_{39}$) of KU : Mn ratio equal to 1 : 1 (figure 2) with the results of the authors quoted above. According to Rocchiccioli-Deltcheff and Thouvenot [11], the symmetric stretch of the $M-O_d$ bond, recorded at $1011\,cm^{-1}$ for the regular structure, is shifted to about $980\,cm^{-1}$ as a result of lower symmetry as a consequence of one terminal atom removal. The introduction of one manganese atom into lacuna should result in the shift of the band toward a higher wave number, as it was observed for Ni (II), Cu (II) and Zn (II) modified lacunary HPW [11]. Raman spectra of the HPW of regular structure, lacunary $NaPW_{11}$ and $NaPW_{11}Mn$ presented in figure 2 indicated the shift of the symmetric stretch of $M-O_d$, which could be expected on the grounds of the cited paper [11].

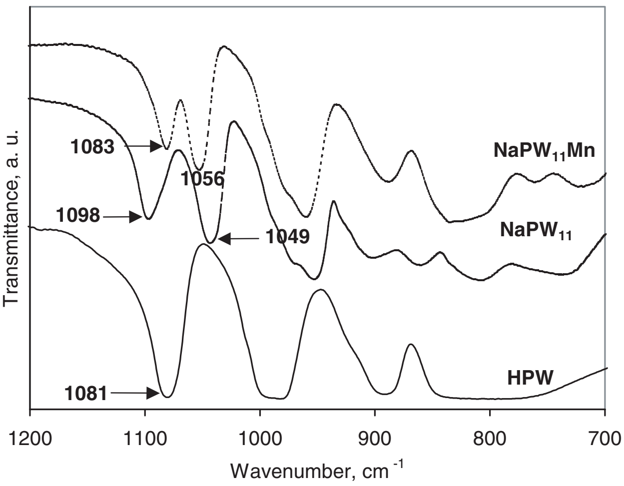

Figure 1. FT-IR spectra of $H_3PW_{12}O_{40}$, $Na_7PW_{11}O_{39}$ and $Na_5PW_{11}MnO_{39}$.

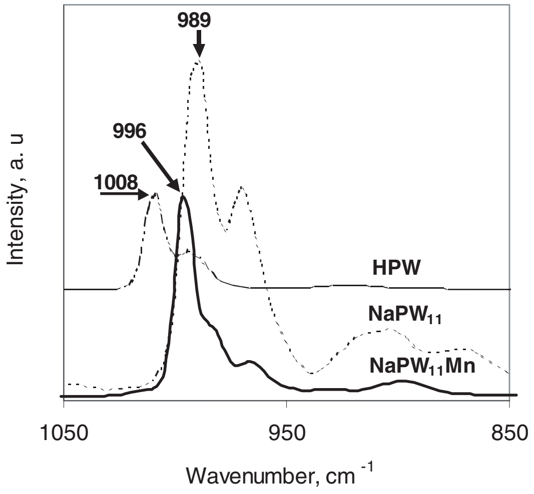

Figure 2. Raman spectra of $H_3PW_{12}O_{40}$, $Na_7PW_{11}O_{39}$ and $Na_5PW_{11}MnO_{39}$.

ESR spectra of manganese-modified $NaPW_{11}Mn_x$ recorded at the X-band showed signals in two ranges: one with $g = \sim 4.3$ and the second with $g = \sim 2$ (figure 3). ESR spectra of $NaHPW_{11}Mn_x$ with $x = 0.1$ or 0.2 showed in the range of $g = \sim 2$, wellresolved six hyperfine lines with parameters: $g = 2.007$ and the hyperfine splitting $A = 8.9\,mT$, $\Delta H_{pp} = 1.3\,mT$ (table 1). The value of ΔH_{pp} showed some broadening of the line resulting from the dipol–dipol interaction, which increased with the increase in the Mn (II) concentration (figure 4). For high concentration of Mn (II) (KU : Mn = 1 : 1), the dipol–dipol interaction was so strong that we were getting a broad line. On this broad line one can see a rather weak spectrum with a hyperfine structure. The parameters for the broad line were $g = 2.007$, A was not resolved and $\Delta H_{pp} = 15\,mT$.

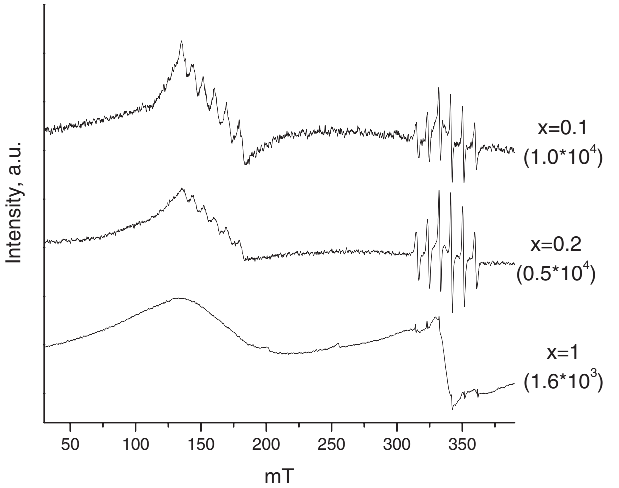

Figure 3. ESR spectra of $NaPW_{11}Mn_xO_{39}(x = 1; 0.1; 0.2)$.

Table 1

The sample	g	A [mT]	Δ H_{pp} [mT]	g	A [mT]	Δ H_{pp} [mT]
$Na_5PW_{11}Mn_1O_{39}$	A: 2.007 B: 2.006	–	~15	~4,3	–	~80
	B: 2.006	9.3	0.5			
$Na_5PW_{11}Mn_{0,1}O_{39}$	2.007	8.9	1.3	A: ~4,3	–	~50
				B: 4.27	8.8	4.8
$Na_5PW_{11}Mn_{0,2}O_{39}$	2.007	8.9	1.4	A: ~4,3	−8.7	~50
				B: ~4.27		4.6
$Na_5PW_{11}Mn_{0,1}O_{39}$–**C**	~2	Very weak signal		~4.3	9.4	5.5
$Na_5PW_{11}Mn_{0,2}O_{39}$–**C**	~2	Very weak signal		~4.27	–	~50
$Cs_5PW_{11}Mn_1O_{39}$	2.007	–	~130	–	–	–
$Cs_5PW_{11}Mn_{0,1}O_{39}$	2.007	9.6	1	4.322	9.2	4.5
$Cs_5PW_{11}Mn_{0,02}O_{39}$	~2	Very weak signal		4.336	9.0	3.6

A – broad line, B – narrow line; for all samples the intensity of A ≫ B

The weak, resolved spectrum had the following parameters: $g = 2.006$, $A = 9.3\,mT$ and $\Delta H_{pp} = 0.5\,mT$ (table 1). These results indicated that only a small amount of Mn (II) was placed in an isolated position in this system (figure 4. The magnitude of hyperfine splitting constant of A_o characterizing the octahedral symmetry of Mn (II) was supposed to be a measure of ionicity of manganese–ligand bond [13,14]. On this basis, considering the A value of ESR signal of Mn (II) complexes with octahedral symmetry (8.9–9.3 mT), the highly ionic bonding between Mn (II) ion and its oxygen ligands could be suggested.

All the spectra of $PW_{11}Mn_x$ samples ($x = 1$, 0.1 or 0.2) recorded in the range of $g =\sim 4.3$ are presented in figure 5. According to Sjoerd Kijlstra *et al.* [15], the Mn (II) line recorded in the range of $g =\sim 4.3$ comes from Mn (II) in the tetrahedral or distorted tetrahedral symmetry. Sample of $PW_{11}Mn_x$ with $x = 1$ showed the broad, unresolved line with $g = 4.3$ and $\Delta H_{pp} = \sim 60\,mT$, while the broad line with marked resolved hyperfine structure of parameters $g = 4.27$, $A = 8.8\,mT$ and $\Delta H_{pp} = 4.8\,mT$ (table 1) was recorded for the samples with lower concentration of Mn (II) ($x = 0.1$ or 0.2).

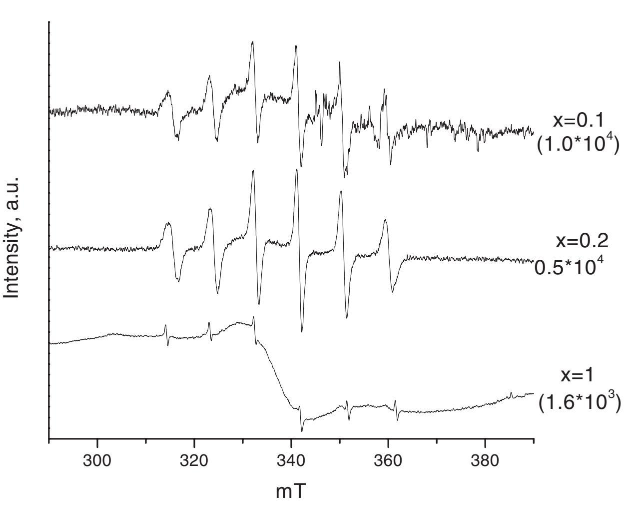

Figure 4. ESR spectra of $NaPW_{11}Mn_xO_{39}$($x = 1$; 0.1; 0.2) in the range of 290–390 mT.

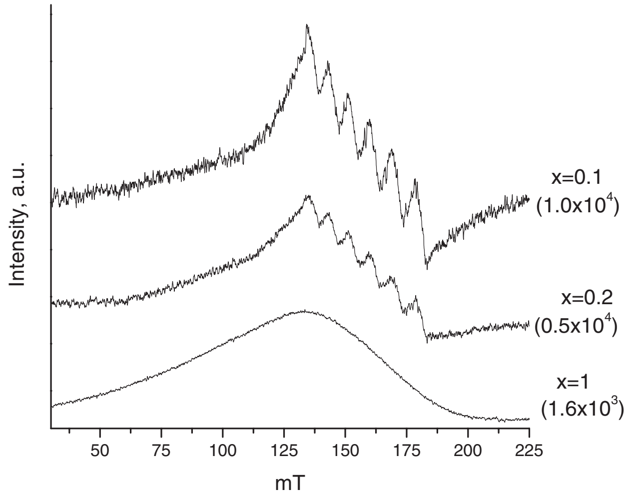

Figure 5. ESR spectra of $NaPW_{11}Mn_xO_{39}$($x = 1$; 0.1; 0.2) in the range of 25 – 225 mT.

The appearance of two signals originating from Mn (II) in ESR spectra of manganese-modified heteropoly compound indicated the presence of two Mn (II) complexes with different symmetry. Mn (II) ion introduced into octahedral lacuna of the Keggin structure should be responsible for the signal in the range of the g parameter of about 2, attributed in the literature to octahedral or distorted octahedral environment [15–18]. Considering the size of Mn (II) ion (0.91 Å for high spin and 0.81 Å for low spin complexes), which is much larger than the size of W (VI) – 0.62 Å, the manganese ion should be located above the equatorial plane formed by four oxygen ions. As a consequence, the distorted symmetry of the Mn (II) ions located in octahedral lacuna should be expected. The geometric constrains should favor the higher oxidation valence for manganese in the Keggin unit. It is consistent with the results of the interaction between $CsPW_{11}MnO_{39}$ and H_2O_2 (at room temperature), leading to a significant decrease in the intensity of the Mn (II) ESR signal at

$g = 2.007$. It could suggest that the part of Mn (II) ions with octahedral symmetry was oxidized to Mn (III), which was not detectable by the ESR technique. Subsequent oxidation under mild conditions did not result in any new signal, which could be assigned to Mn (IV). These results showed that Mn (II) was oxidized to Mn (III) but not to Mn (IV), which was consistent with results reported by Pope [4], indicating that Mn (II) introduced into lacuna of $PW_{11}O_{39}$ could be oxidized only to Mn (III).

According to Pope and Müller [19] and also Okuhara and Misono [20], cations present in solid heteropoly salts and neutralizing the negative charge of heteropoly anions neighbor with two Keggin units. Coordination of cations (in our samples of Mn (II) ions) can be completed by molecules of water. Therefore, it seems reasonable to ascribe the ESR signal recorded for the studied samples in the range of $g = 4.3$ to Mn (II) in cationic position. This point of view may be confirmed by the change of intensity of ESR signals, which results from calcination at 400 °C. Calcination of the samples at 400 °C led to a decrease in the intensity of the signal with $g =\sim 2$ and simultaneously to an increase in the intensity of the signal with $g = 4.3$ (figure 6 and 7). Decrease in the intensity of the line at $g = 2.007$ may originate both from oxidation of part of Mn (II) ions located in octahedral lacuna to Mn (III) and from transformation of lacunary Keggin structure to the regular Keggin unit as a result of thermal treatment. The FT-IR spectra of freshly prepared $Na_5PW_{11}MnO_{39}$ showed characteristic splitting of the P–O bond (1083 and 1056 cm^{-1}) coming from the lower symmetry of the central atom environment. It resulted from exchange of terminal tungsten atom to manganese (II). Analysis of FT-IR spectra of the sample calcined at 400 °C indicated the partial transformation of the lacunary structure to the regular Keggin unit (figure 6). The transformation of lacunary $NaPW_{11}Mn$ to regular $NaPW_{12}$ structure was reported by Gamelas *et al.* and it was confirmed by FT-IR and ^{31}P NMR spectra [21]. The transformation should result in the release in part of Mn (II) ions from octahedral lacuna of heteropoly anions. Considering simultaneous increase in intensity of the signal of $g = 4.3$, one can suppose that Mn (II) ions located in cationic position show symmetry characterized by this signal (of $g = 4.3$). Distorted tetrahedral symmetry of Mn (II) cations characterized by the ESR signal in the low range of the magnetic field was reported for Mn (II) ions exchanged into ZSM-5 zeolite channels as well as for extra framework Mn (II) located in the channels of MCM-41 mesoporous sieves [17].

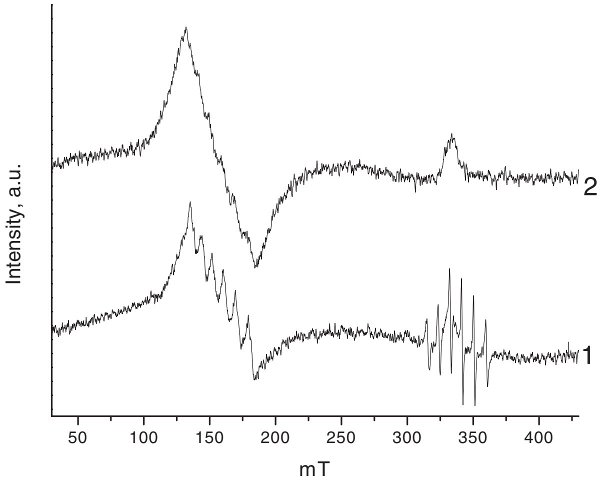

Figure 6. ESR spectra of $NaPW_{11}Mn_{0.1}O_{39}$: 1. as synthesized, 2. after calcination at 400 °C.

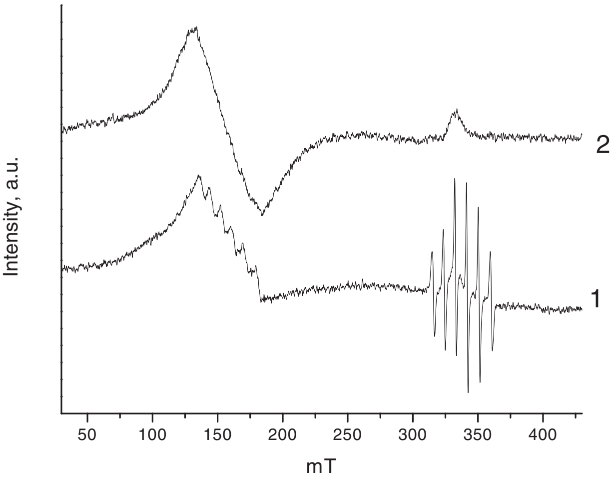

Figure 7. ESR spectra of $NaPW_{11}Mn_{0.2}O_{39}$: 1. as synthesized, 2. after calcination at 400 °C.

Calcination of $NaPW_{11}Mn_x$ samples at 400 °C also led to the disappearing of the hyperfine structure of the line with $g = 4.3$ (figures 6 and 7). This indicated that manganese ions located in isolated places migrated toward each other owing to dehydration [22], which resulted in stronger dipol–dipol interaction.

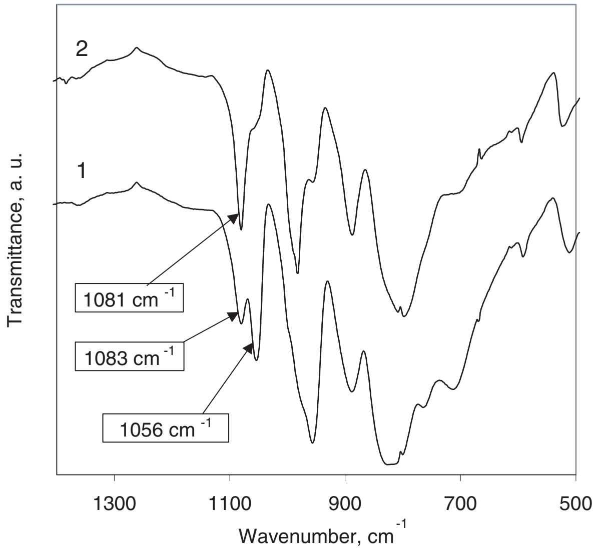

Figure 8. FT-IR spectra of $NaPW_{11}MnO_{39}$: 1. as synthesized, 2. after calcination at 400 °C.

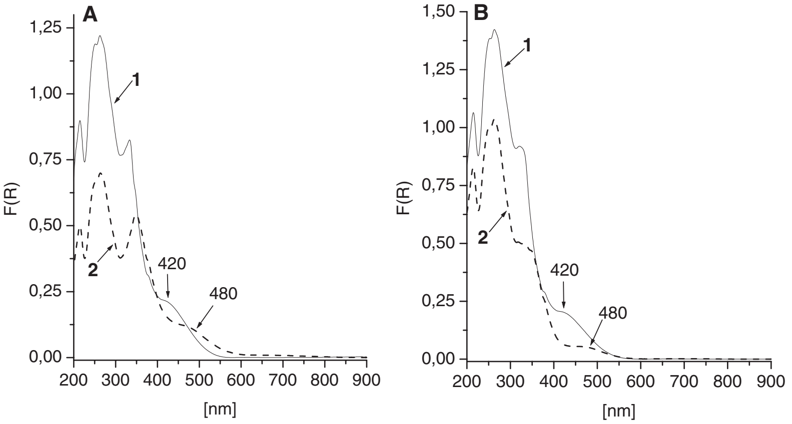

Figure 9. UV–vis spectra of (**A**) $NaPW_{11}Mn_{0.2}O_{39}$ and (**B**) $NaPW_{11}Mn_{0.1}O_{39}$: 1. as synthesized, 2. after calcination at 400 °C.

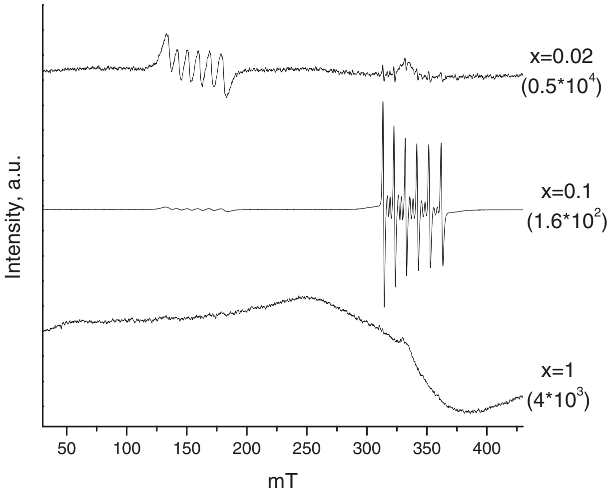

Figure 10. ESR spectra of $CsPW_{11}Mn_xO_{39}$ ($x = 1; 0.1; 0.02$).

Diffusion reflectance spectra in the UV–vis region recorded for uncalcined and calcined samples showed the weak bands at about 420 and 480 nm respectively (figure 9). The first one was ascribed to the presence of Mn (II) ions [16], while the band at 480 nm could be attributed to the presence of Mn (III) or Mn (IV) ions [15,23]. Considering that the ESR spectra did not provide any evidence for Mn (IV) ions in the system, it seems justified to assume that the thermal treatment at 400 °C resulted in partial oxidation of Mn (II) to Mn (III) ions. In spite of the concentration of Mn (II) in modified heteropoly anions being much higher than Mn (III), the last one was mainly observed in the UV–vis spectra, because of pronounced absorption, resulting from the spin-allowed transition $^5E_g \rightarrow {}^5T_{2g}$. The transitions for the $3d^5$ configuration of Mn (II) are spin-forbidden, which results in very low UV absorption [14].

Considering that the large cations ($[NBu_4]^+$ or Cs^+) may enforce high cubic symmetry for the Keggin units packing [24], the cesium salt of manganese-modified $PW_{11}Mn$ was synthesized. ESR spectra of $CsPW_{11}Mn_xO_{39}$ showed both signals: in the low magnetic field range ($g = \sim 4.3$) and in the high range ($g = \sim 2$) as well (figure 10). A strong, unresolved signal at $g = \sim 2$ was recorded for the stoichiometric sample (KU : Mn = 1 : 1). With decrease in the manganese concentration (KU : Mn = 1 : 0.1), the signal became well resolved and showed forbidden transitions. For the concentration of Mn (II) with respect to the ratio KU : Mn = 1 : 0.02, only a very weak signal at $g = \sim 2$ was recorded, while the low field signal with $g = 4.3$, $A = 9\,mT$ and $\Delta H_{pp} = 3.6\,mT$ became well pronounced.

4. Summary

ESR spectra of alkali salts of manganese-modified lacunary heteropoly anion $PW_{11}M_xO_{39}$ showed that Mn (II) ions may be located both in octahedral lacuna and in the cationic position even for very low concentration of manganese ions. Intense, unresolved signal of $g = \sim 2$, observed for high concentration of Mn (II) ions seems to be due to distorted octahedral symmetry of Mn (II) ions located in octahedral lacuna of defected heteropoly anion. Mn (II) ion characterized of low field signal with $g = 4.3$, with usually well-resolved hyperfine structure, seems to be located in cationic position similarly as it was observed for extra framework Mn (II) ions accommodated in the channels of molecular sieves.

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