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Spectroscopic and magnetic studies of new vanadyl tungstophosfate and tungstoarsenate with an open well-Dawson structures

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The $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\{K(H_2O)_2\}(P_2W_{18}O_{66})]$ **(1)** and $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\{K(H_2O)_2\}(As_2W_{18}O_{66})]$ **(2)** complexes were prepared and investigated through spectroscopic (FT-IR, UV-VIS, ESR) methods and magnetic susceptibility measurements. The analysis of the coordination mode of the vanadium ions was made by comparing the FTIR spectra of the complexes **(1)** and **(2)** with those of the $K_{11}[\{K(H_2O)_3\}_2\{K(H_2O)_2\}(P_2W_{18}O_{66})$ and $K_{11}[\{K(H_2O)_3\}_2\{K(H_2O)_2\}(As_2W_{18}O_{66})$ ligands. The shift of ν_{as}(W-O_e-W) and ν_{as}(W-O_c-W) vibrations bands shows the coordination of each vanadyl ion at oxygen atoms from the belt region.The UV electronic spectra of the complexes and of the ligand contain one bands characteristic for the ligand to metal charge transfer in the heteropolyanion cage. The visible electronic spectra of both complexes in aqueous solution are tipicaly for vanadyl ions in C_{4v} environment. Powder EPR spectra obtained in the X band contains two Gaussian components, one axial and another isotropic, in the 2:3 ratio. The simulation of the experimental spectra indicate the trapping of the unpaired electrons at the parent V^{IV} paramagnetic ions and the absence of direct delocalization towards the neighboring vanadium ions. The very broad component observed in the EPR spectra are proofs for the existence in both samples of dipolar coupled vanadium(IV) ions.

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Keywords: Clusters, FTIR, UV-VIS, EPR Spectroscopy

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1. Introduction

Interest in polyoxometalates is increasing worldwide due to the enormous variety of structures leading to interesting and often unexpected properties in fields such as nanomaterials, catalysis, magnetochemistry and medicinal applications [1-3]. At the same time it must be pointed out that the mechanism of formation of polyoxometalates is not well understood and commonly described as self-assembly.

Wells–Dawson polyoxometalates are an important class of polyoxoanions constituted by the formal association of two fragments of Keggin type anions via condensation reactions.

From these 8 complete 9 anions, mono-, di-, tri- and hexavacant species can be obtained by selective hydrolysis reactions and are precursors of a very large number of derivatives with transition metal cations. These complexes have attracted considerable attention over the past years as models of oxide surfaces, precursors for synthesis of organometallic derivatives, for their magnetic properties and as homogeneous catalysts and electrocatalysts. To date, Wells–Dawson anions $[X_2M_{18}O_{62}]^{6-}$ are known with M = Mo or W and X = P (V) or As (V) in aqueous solution and S (VI) in non aqueous solution. On the contrary, only Keggin type polyoxoanions are known with X = Si (IV) even if a priori nothing precludes the formation of Wells–Dawson tungstosilicates. Here we report the synthesis, molecular structure and reactivity of α-$[As_2W_{18}O_{66}]^{14-}$, which is an intermediate between the monomer A-α-$[AsW_9O_{34}]^{9-}$, and the hypothetical a A-α-$[As_2 W_{18}O_{62}]^{8-}$ Wells–Dawson anion (Fig. 1).

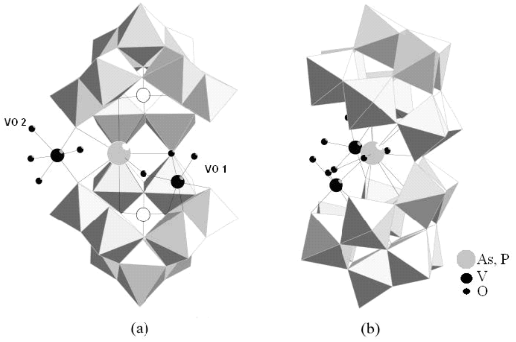

Fig. 1. Polyhedral representation of the $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\{K(H_2O)_2\}(As_2W_{18}O_{66})]\cdot 25H_2O$, front view(a) side view (b).

The $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\{K(H_2O)_2\}(P_2W_{18}O_{66})]$ **(1)** and $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\{K(H_2O)_2\}(As_2W_{18}O_{66})]$ **(2)** complexes were prepared and investigated through spectroscopic (FTIR, UV-VIS, ESR) methods and magnetic susceptibility measurements.

2. Experimental section

Synthesis of $K_8[HPW_9O_{34}]\cdot 20H_2O$ (L_1)

12 g $K_2WO_4\cdot 2H_2O$ was dissolved in 15 ml of distilled water, and 0.3 ml H_3PO_4 85% was added successive driping, after that 2.28 ml CH_3COOH 96% was added. The crystallization starts immediately when we obtain an microcrystal precipitate white, and the solution is filtrated immediately. White crystals appear.

Synthesis of $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\}\{K(H_2O)_2\}(P_2W_{18}O_{66})]$ (1)

Synthesis of $(VO)P_2W_{18}O_{66}$, pH=4

0.32 g $(VO)SO_4\cdot$ 2 H_2O was dissolved in 23 ml of distilled water, under powerful agitated are added 4.46 g $Na_8[HPW_9O_{34}]\cdot 20H_2O$. Was observed that the colour blue is changing to brown very dark and is forming a precipitate. This solution is let to agitate about 30 minutes, than is added 2.5g KCl under the persist agitate. After that the resulted solution was let in the refrigerator all night. Next day was observed that in the solution appear a precipitate with an powder aspect. The solution was filtrated. The precipitate have a brown colour and the filtrate have pH=4. After fourteen days in the solution appear crystals which were filtrate and were put to dry. The crystals have a dark blue colour. Between the crystals are ligand scrapings.

Synthesis of $(VO)P_2W_{18}O_{66}$, pH=1.5

For this synthesis was use the same substances and quantity that was use in the first synthesis but it was worked at pH=1.5. 0.32 g $(VO)SO_4\cdot$ 2 H_2O was dissolved in 23 ml of distilled water, under powerful agitated are added a few HCl spray to obtain the pH=1.5, after that was added 4.46 g $Na_8[HPW_9O_{34}]\cdot 20H_2O$. Was observe that the color blue is changing to brown very dark. This solution is let to agitate about 30 minutes, than is added 2.5g KCl under the persist agitate. The solution was filtrated. The precipitate have a brown colour and the filtrate have pH=1.5. After that the resulting solution was let at the room temperature all night..After two days in the solution appear crystals. The solution was filtrated and the crystals were let to dry. The crystals have a dark blue colour. After four days were observe in the remaining solution new small crystals and this were filtrated again and were the crystals let to dry. The crystals have a dark blue color.

Synthesis of $(VO)P_2W_{18}O_{66}$, pH=7

For this synthesis was use the same substances and quantity that was use in the first synthesis but it was worked at pH=1.5 . 0.32 g $[VO]SO_4\cdot 2$ H_2O was dissolved in 23 ml of distilled water, under powerful agitated are added a few Na_2CO_3 spray to obtain the pH=7. Was observ that the colour blue is changing to grey to blue milky,after that was added 4.46 g $Na_8[HPW_9O_{34}]\cdot 20H_2O$. Than was observe that the color grey to blue milky is changing to very dark violet. This solution is let to agitate about 30 minutes, than is added 2.5g KCl under the persist agitate. The solution was filtrated. The precipitate have a brown colour. The filtrate have pH=7. After that the resulting solution was let in the refigerator all night. Next day in the solution appear crystals. The solution was filtrated but the crystals were lost,and the remaining filtrate never made crystals.In this case was obtain just an powder precipitate.

Synthesis of $K_8[HAsW_9O_{34}]\cdot 18H_2O$ (L_2)

A mixture of 10 g $K_2WO_4\cdot 2H_2O$ and 1.05g $Na_2HAs4O\cdot 7H_2O$ was dissolved in 10 ml distilled water and agitated at 40 ºC temperature. After that 1.5 ml CH_3COOH 96% was added successive driping. The crystallization starts immediately when we obtain an microcrystal precipitate white. The solution will be filtrated at vacuum. The crystals are washed with 5 ml acetone. White crystals appear.

Synthesis of $K_9[\{VO(H_2O)_4\}\{VO(H_2O)\}\{K(H_2O)_2\}(As_2W_{18}O_{66})]$ (2)

Synthesis of $(VO)As_2W_{18}O_{66}$, pH=4

0.32 g $[VO]SO_4\cdot 2$ H_2O was dissolved in 23 ml of distilled water, under powerful agitated are added 4.46 g $Na_9[AsW_9O_{34}]\cdot 11H_2O$.Was observ that the colour blue is changing to brown very dark and is forming a precipitate. This solution is let to agitate about 30 minutes,than is added 2.5g KCl under the persist agitate,when the colour is changing to the colour of the coffe. The solution was filtrated. The precipitate have a lihgt brown colour and the filtrate have pH=4. After that the resulting solution was let at the room temperature all night. Next day in the solution doesn`t appear cristals. The precipitate has a mud aspect. After eight days were formed some crystals, and the solution was filtrated, the filtrat has the coloure dark green ,but the crystals are KCl. In this case was not obtain crystals just an precipitate,who has a light brown colour.

Synthesis of $(VO)As_2W_{18}O_{66}$, pH=1.5

For this synthesis use the same substances and quantity that was use in the first synthesis but was worked at pH=1.5. 0.32 g $[VO]SO_4\cdot 20HO_2$ was dissolved in 23 ml of distilled water, under powerful agitated are added a few HCl spray to obtain the pH=1.5, after that was added 4.46 g $Na_9[AsW_9O_{34}]\cdot 11H_2O$. Was observe that the color blue is changing to brown very dark. This solution is let to agitate about 30 minutes, than is added 2.5g KCl under the persist agitate, when the colour is changing to the colour of the coffe. The solution was filtrated. The precipitate have a light brown colour and the filtrate have pH=1.5. After that the resulting solution was let at the room temperature all night. Next day in the solution doesn`t appear crystals. The precipitate has a mud aspect. After three weeks were formed black crystals.

Synthesis of $(VO)As_2W_{18}O_{66}$, pH=7.5

For this synthesis was use the same substances and quantity that was use in the first synthesis but it was worked at pH=7.5. 0.32 g $[VO]SO_4\cdot SO_4$ was dissolved in 23 ml of distilled water, under powerful agitated are added a few Na_2CO_3 spray to obtain the pH=7.5, after that was added 4.46 g $Na_9[AsW_9O_{34}]\cdot 11H_2O$. Was observe that the color blue is changing to brown very light. This solution is let to agitate about 30 minutes, than is added 2.5g KCl under the persist agitate, when the colour is changing to the colour of the coffe. The solution was filtrated. The precipitate have a lihgt brown colour and the filtrate have pH=7. After that the resulting solution was let at the room temperature all night. Next day in the solution does not appear crystals. The precipitate has a mud aspect. In this case was not obtain crystals just an precipitate,who has a light brown colour.

3. Results and discussion

3.1 Chemical analysis

The composition in vanadium, potassium phosphorus and arsenicum of each complex was determined by atomic absorption. The water content was estimated on the basis of thermal measurements by heating of the samples at 120 ºC and at 45 ºC for 30minutes.

The study of the new vanadyl tungstophosphates' and tungstoarsenates' thermal behavior reveals that complexes contain 35, respectively 32 water molecules. For $(VO)_2P_2W_{18}O_{66}$, at 120 ºC 28 crystallization water molecules were loss and at 450 ºC 7 coordination water molecules were loss, and for $(VO)_2As_2W_{18}O_{66}$, at 120 ºC 25 crystallization water molecules were loss and at 450 ºC 7 coordination water molecules were loss (Table 1).

Table 1. Analytical data of the synthesized compounds.

Compound	%									
	K		V		W		X		H_2O	
							P	As		
	calc	found	calc	found	calc	Found	calc	found	calc	found
1	7.05	6.88	1.84	1.78	59.66	59.45	1.12	1.10	10.71	10.60
2	7.46	7.30	1.94	1.88	63.10	62.98	2.85	2.88	10.29	10.22

3.2 FT-IR spectra

FT-IR spectra were recorded on a Jasco FT/IR 610 spectrophotometer in the 4000–400 cm^{-1} range, using KBr pellets. EPR spectra on powdered solids were recorded at r.t. at *ca.* 9.6 GHz (X band) using a Bruker ESP 380 spectrometer.The IR spectra of the synthesized complexes and the **AsW_9** respectively **PW_9** ligands are plotted in Fig. 2,3 and in Table 2.

Table 2. IR spectral data (cm^{-1}).

Band	L_1	1	L_2	2
$\nu_{as}(X\text{-}O_i)$	1056.80vs 1014.37s	1089.58s 1062.59s	875.42sh	904.45vs
$\nu_{as}(W{=}O_t)$	935.31 vs	962.30vs	973.88sh; 941.09s	980.02s
$\nu_{as}(W\text{-}O_c\text{-}W)$	885.17s	894.61s	875.42sh 842.74vs	904.45vs 848.53s
$\nu_{as}(W\text{-}O_e\text{-}W)$	811.88vs;b 759.82vs	794.53vs;b 736.67 sh	796.46m; 750.17s	784.89vs; 740 sh;

w, weak; m, medium; s, strong; vs, very strong; sh, shoulder;b, board; O_i is the oxygen which links the As, P and W atoms, $O_{c,e}$ connect corner and edge-sharing octahedra, respectively, O_t is a terminal oxygen.

The analysis of the coordination mode of the vanadium ions was made by comparing the FT-IR spectra of the complexes $(VO)_2P_2W_{18}O_{66}$ and $(VO)_2As_2W_{18}O_{66}$ with those of the ligands. The stretching vibration of the terminal $W{=}O_t$ bonds is slightly shifted towards higher wavenumbers in the FTIR spectra of the complexes, which indicates the non-involving of the terminal bonds in the coordination to the vanadium ions. The $\nu_{as}(W{=}O_t)$ vibration band is broader in the complex **(1)** spectrum than the corresponding band in the ligand spectrum because of its superposition with the stretching vibration $\nu_{as}(V{=}O)$ [4]. The equivalence of the V=O groups in the complex **(1)** makes the corresponding vibration bands to be broad and unsplitted. On the other hand, two $\nu_{as}(V{=}O)$ vibration bands at 961 and 988 cm^{-1} are clearly separated from the $\nu_{as}(W{=}O_t)$ band in the complex **(2)** FT-IR spectrum. This is due to the presence of mixed valence V^{IV}/V^{V} ions [5-6].

The tricentric $W–O_e–W$ bonds of the edge-sharing WO_6 octahedra have different stretching vibrations in the two complexes. The $\nu_{as}(W–O_e–W)$ vibration is blue shifted with 3 cm^{-1} in the complex **(2)** FT-IR spectrum compared to the ligand spectrum, but red shifted with 14 cm^{-1} in the complex **(1)** FT-IR spectrum. This behavior arrises from different deformations induced by the vanadium ions coordination in the frame of the trilacunary ligands. The decrease of the $\nu_{as}(W–O_e–W)$ frequency in the complex **(2)** indicates the lengthening of these bonds after the metallic ion complexation [7]. The small increase of this frequency in the complex **(2)** is in agreement with the coordination to the ligand of the ions V^{IV} and V^{V} with lower oxidation state than the addenda ions W^{VI} of the heteropolyanion [8].

All the characteristic stretching vibrations appearing in 1000-700 cm^{-1} range are shifted in complexes towards higher frequencies than in ligands, that is consistent with an increase of the anion cohesion when coordination of the vanadyl ions in the polyoxometalate framework occurs, excepting the last bands which are shifted in complexes towards lower frequencies than in ligands is consistent with a decrease of the anion cohesion when coordination of the vanadyl ions in the polyoxometalate framework occurs.

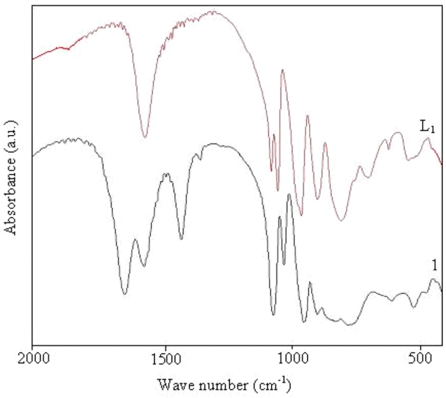

Fig. 2. FT-IR spectra of the L_1 ligand and complex 1.

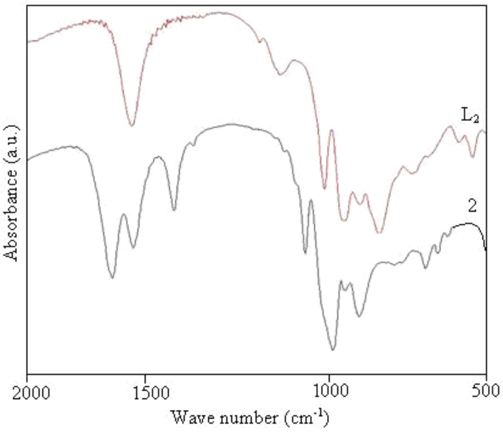

Fig. 3. FT-IR spectra of the L_2 ligand and complex 2.

3.3 Electronic spectroscopy

Electronic spectra were performed in aqueous solutions within a range of λ = 190–1000nm on an ATI Unicam-UV-Visible spectrophotometer with Vision Software V 3.20.

The UV electronic spectra of the complexes and of the ligand (Fig. 4) contain one bands characteristic for the ligand to metal charge transfer (LMCT) in the heteropolyanion cage. The band at lower wavelength for the $p\pi(O_t) \rightarrow d\pi^*(W)$ transitions [9] appears at the same wavelength (193.6 nm) in the ligand spectrum as well as in the complexes spectra. Because of the broadening of these bands, their positions have been estimated from the first derivative of the spectrum. The charge transfer transition is situated at ≈ 254 nm in the ligand spectrum, shifted towards higher energies in the complex **(1)** (at ≈ 253 nm), but at lower energies in the complex **(2)** (at ≈ 255 nm).

The visible electronic spectra of both complexes show a relative stronger absorption above 16000 cm^{-1} and a band with a shoulder at lower wave numbers (Fig. 5). The strong absorptions correspond to the $V^{IV} \rightarrow W^{VI}$ charge transfer transitions [10]. The Gaussian analyses of the spectra lead to obtaining the position of the bands for V^{IV} ions d-d transitions. The two bands appear at 12040 cm^{-1} and 14705 cm^{-1} for the complex **(1)** and at 12410 cm^{-1} and 15915 cm^{-1} for the complex **(2)**. The bands of each complex are related to the $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ (I) and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ (II) transitions in the Ballhausen and Gray molecular orbital theory for vanadyl ions in C_{4v} local symmetry [11]. The higher energies for the complex **(2)** are related to different degrees of delocalization of the unpaired electrons from the parent vanadium ions towards the neighboring oxygens, by means of out-of plane π bondings and in-plane σ-bondings, respectively.

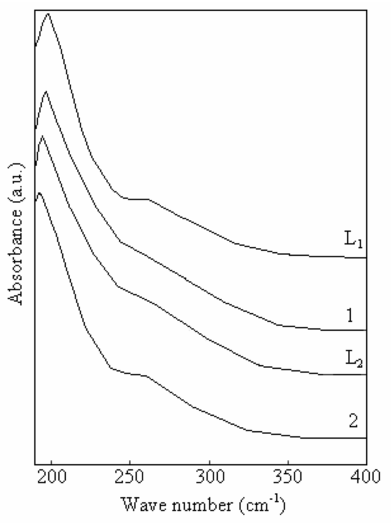

*Fig. 4. UV spectra of synthetized ligands and complexes obtained aqueous solutions: ligand **L_1** and complex **1**; ligand **L_2** and complex **2** .*

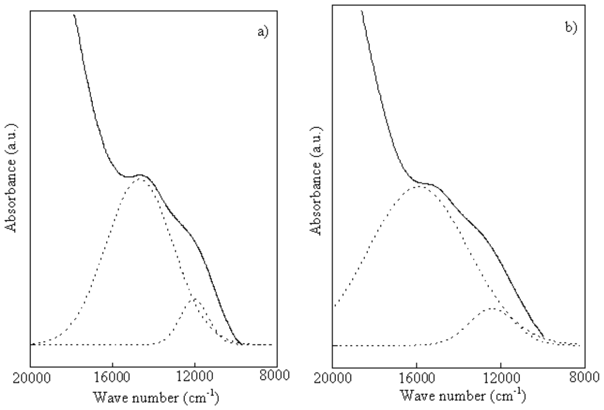

Fig. 5. The electronic spectra in visible of the polyo xometalate complexes.

3.4 EPR spectra

Powder EPR spectrum of the complex (**1**) (Fig. 6a), obtained in the X band at r.t. contains a series of signals superposed on a very broad component. Such types of spectra were previously reported for other HPOM involving vanadium ions [5,12]. For the interpretation of the obtained spectrum, it was simulated as a superposition of two Gaussian components, one axial and another isotropic, in the 2:3 ratio (Fig. 6a).

EPR parameters of the axial component, derived from the simulation, are: $g_{II} = 1.896$, $g_{\perp} = 1.972$, $A_{II} = 184$ G, $A_{\perp} = 69$ G and the linewidths $\Delta B_{II} = 57$ G, $\Delta B_{\perp} = 32$ G for a Gaussian lineshape. The principal axes of the ***g*** and ***A*** tensors were presumed to be coincident. The hyperfine structure of the complex containing eight lines in each of the parallel and perpendicular bands indicates the fact that the unpaired electrons of the three V^{IV} ions are prevalently trapped on the parent ions. For the assignement of the isotropic component, characterized by $g_{iso} = 1.972$ and ΔB_{iso}(p-p) = 500 G we took into account the fact that polyoxometalates with more vanadium ions present such broad EPR signals with a resolved hyperfine structure either due to the electron hopping between the vanadium ions in a thermally activated process or to a clustered system in undiluted powder samples [13-15]. The intermetallic distance longer than 4.2 Å prevents the direct electron hopping between the vanadium ions. The broad component of the spectrum could be interpreted in therms of the presence of very weak extended exchange interactions within the vanadyl triangular cluster, as recently reported for the sandwich-type complex with Sb^{III} [16]. These lead to the appearance of two doublets ($S = 1/2$) and an excited quartet ($S = 3/2$). This last state togheter with the presence of dipolar interactions between the vanadium ions and the unsolved hyperfine structure and possible *g* and *A* tensors anisotropies could be responsible for the appearance of the broad component of the spectrum.

The powder EPR spectrum of the complex **(2)** also exhibits two components in the 2:3 ratio. EPR parameters obtained for the axial component by simulating the spectrum are the spin state S = 1/2, $g_{II} = 1.908$, $g_{\perp} = 1.968$, $A_{II} = 186$ G, $A_{\perp} = 60$ G and the linewidths $\Delta B_{II} = 46$ G, $\Delta B_{\perp} = 28$ G. These parameters belongs to each vanadium(IV) ion. The isotropic component has $g_{iso} = 1.968$ and $\Delta B_{iso} = 500$ G and suits from dipolar coupling of the vanadium ions. Using the EPR parameters, the molecular coefficient $\beta_2^2 = 0.907$ and the Fermi contact term K = 0.662 have been calculated. σ bonds.

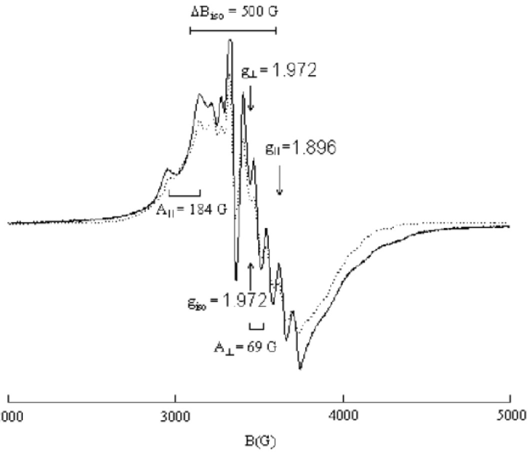

*Fig. 6. Powder EPR spectrum of the complex **1**.*

4. Conclusions

There were preparated two compounds **(1)** and **(2),** for who we propose a Wells-Dawson structure, but after the chemical analysis and spectrometrical measurements we observe that for those compounds correspond an open Wells-Dawson structure.

The compounds were characterized with chemical analysis, spectrometrical measurements in UV-Vis, EPR and IR

The results of the chemical analysis are well concordant to the calculated one.

FT-IR Spectra. All the characteristic stretching vibrations appearing in 1000-700 cm^{-1} range are shifted in complexes towards higher frequencies than in ligands, that is consistent with an increase of the anion cohesion when coordination of the vanadyl ions in the polyoxometalate framework occurs, excepting the last bands which are shifted in complexes towards lower frequencies than in ligands is consistent with a decrease of the anion cohesion when coordination of the vanadyl ions in the polyoxometalate framework occurs.

The spectroscopic and electrochemical investigation of the **(1)** and **(2)** complexes indicate the coordination of the vanadium ions at two corner-sharing octahedra from each α-A-$[AsW_9O_{33}]^{9-}$ respectively α-A-$[PW_9O_{33}]^{9-}$ heteropolyanion.

EPR Spectra.EPR parameters obtained after the simulation of the experimental spectra of the complexes **(1)** and **(2)** indicate the trapping of the unpaired electrons at the parent V^{IV} paramagnetic ions and the absence of direct delocalization towards the neighboring vanadium ions. The very broad component observed in the EPR spectra are proofs for the existence in both samples of dipolar coupled vanadium(IV) ions.

UV Spectra. The UV electronic spectra of the complexes and of the ligand contain one bands characteristic for the ligand to metal charge transfer (LMCT) in the heteropolyanion cage.The visible electronic spectra of both complexes show a relative stronger absorption above 16000 cm^{-1} and a band with a shoulder at lower wave numbers. The strong absorptions correspond to the $V^{IV} \rightarrow W^{VI}$ charge transfer transitions.

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