Synthesis and Physical-Chemical Study of Two Sandwich-Type Heteropolyoxometalates With Dinuclear Vanadium Clusters

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Abstract

The sandwich-type $K_{12}[(VO)_2Sb_2W_{20}O_{70}] \cdot 31H_2O$ (**1**) and $K_{11}[(VO)_2Bi_2W_{20}O_{70}] \cdot 21H_2O$ (**2**) heteropolyoxotungstates were investigated by means of elemental analyses, thermogravimetric and spectroscopic (FT-IR, UV–VIS and EPR) methods.

The analysis of vanadium ions coordination mode was made comparing the FT-IR spectra of the complexes **1** and **2** with the $K_{12}[Sb_2W_{22}O_{74}(OH)_2] \cdot 38H_2O$ (**L$_1$**) and $K_{12}[Bi_2W_{22}O_{74}(OH)_2] \cdot 40H_2O$ (**L$_2$**) ligands. FT-IR spectra of the complexes show the presence of the V=O bonds characterized by $\nu_{as}(V=O)$ vibrations. In both complexes, the coordination of the vanadium shifts the $\nu_s(W–O_{c,e}–W)$ vibration bands.

In UV spectra, the charge transfer $p_\pi(O_{c,e}) \rightarrow d_{\pi*}(W)$ band is shifted in complexes compared to the ligands spectra with $\approx$ 245 nm for **1** towards higher wavelength and with $\approx$ 250 nm for **2** towards lower wave numbers.

Visible spectra contain $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ transition bands for vanadyl ions in C_{4v} local symmetry, at 12020 cm^{-1} respectively 14710 cm^{-1} for the complex **1**, and at 12405 cm^{-1} and 15905 cm^{-1} for the complex **2**. The powder EPR spectra at room temperature exhibit eight components both in the perpendicular and in the parallel bands and are typical for mononuclear oxovanadium species in axial environment.

Keywords: Heteropolyoxotungstates, VO complexes, FT-IR spectroscopy, UV-VIS spectroscopy, EPR spectroscopy

1. Introduction

During the last years, interest for heteropolyoxometalates (HPOM) substituted by early transition metals (3d) has been continuously growing.[1–3] These complexes have the capacity to include more transition metals, which interact by means of dipolar or exchange coupling.[4,5] This aspect recommends heteropolyoxometalates as potential hosts of high dimensional clusters.[3, 4, 6, 7]

A special class of heteropolyoxometalates is the unsaturated trilacunary Keggin-type $[X^{n+}W_9O_{33}]^{(12-n)-}$ structure, where the heteroatom X is one of the Bi^{III}, As^{III} or Sb^{III} ions.[8–10] The main characteristic of these ions is the presence of one pair of electrons, which prevents further

condensation to a saturated Keggin structure.[8] However, transition metal ions could link the lacunary units, resulting a sandwich-type structure. During the last decade syntheses and structural characterization of a series of dimeric polyoxotungstates containing Sb^{III} and Bi^{III} as subvalent heteroatom have been reported, the chemistry of heteropolyoxotungstates being a new, but expanding field of research. Were synthesized compounds containing transition-metals: $[M_2Sb_2W_{20}O_{70}(H_2O)_2]^{10-}$, where M^{n+}=Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, $[M_2Bi_2W_{20}O_{70}(H_2O)_2]^{10-}$, where M^{n+}=Fe^{3+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, and also a series of Sn^{II} compounds.[3]

In this work we investigate the new $K_{10}[(VO)_2Sb_2W_{20}O_{70}] \cdot 20H_2O$ (**1**) and $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$
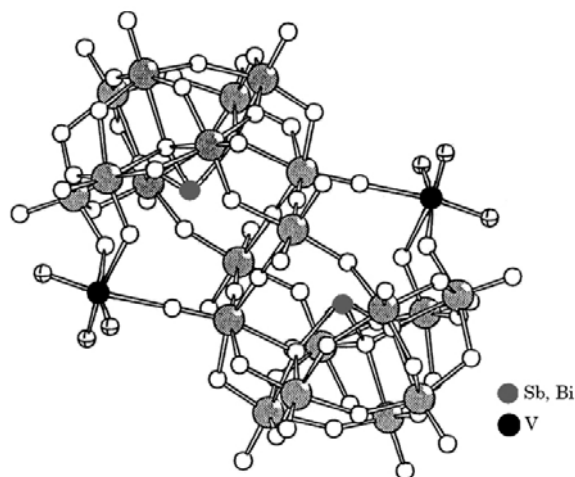
Fig. 1 The structure of the complexes $[X_2(VO)_2W_{20}O_{70}(H_2O)_4]^{10-}$, X=Sb, Bi.[11]

(**2**) sandwich-type complexes by spectroscopic (FT-IR, UV–Vis, EPR) methods.

The main goal was to obtain information about the vanadium ions coordination to the trilacunary ligand, the local symmetry around the vanadium ions and the presence of possible vanadium–vanadium couplings.

The investigated compounds contain two identical β-B-$[XW_9O_{33}]^{9-}$ heteropolyanion fragments, X=Sb^{III}, Bi^{III} related by a center of inversion and facing each other with their open sites (Fig. 1).[11–14]

A belt of two vanadium ions connects the trilacunary anions.[3, 15] Formally, the *fac*-WO$_3$ groups have been exchanged for transition-metal ions with three aqua molecules as ligand. This unusual formation leads to three free coordination sites at the transition-metal atoms that are completed by water molecules.

2. Experimental Section

All chemicals were of reagent grade and used without further purification. The $[SbW_9O_{33}]^{9-}$ unit have been synthesized as previously described.[1]

Synthesis of K$_{12}$[Sb$_2$W$_{22}$O$_{74}$(OH)$_2$] · 38H$_2$O (L$_1$)

The sodium salt of $[SbW_9O_{33}]^{9-}$ [1] (10 g, 3.49 mmol) and Na$_2$WO$_4$ · 2H$_2$O (2.3 g, 6.99 mmol) were dissolved in distilled water (10 mL) while gently heated. By drop wise addition of 1 M HCl (23.5 mL) the pH of the reaction mixture was set to 4–5; the mixture was then evaporated to one third of its volume. After cooling, the sodium salt of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ was formed with a yield of 6.7 g (63%). Crystals of K$_{12}$[Sb$_2$W$_{22}$O$_{74}$(OH)$_2$] · 38H$_2$O were obtained after recristallization of this compound with KCl (2.68 g, 35.9 mmol) in water (10 mL) by diffusion techniques. The compound was characterized by IR spectrum.

Synthesis of K$_{10}$[(VO)$_2$Sb$_2$W$_{20}$O$_{70}$] · 20H$_2$O (1)

The salt of $[(VO)_2Sb_2W_{20}O_{70}]^{10-}$ was prepared by the reaction of stoichiometric amounts of K$_{12}$[Sb$_2$W$_{22}$O$_{74}$(OH)$_2$] · with the transition-metal salt (VO)SO$_4$ · 2H$_2$O. The potassium salt of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (2 g, 0.3 mmol) prepared above was suspended in 40 mL Na-OAc/HOAc buffer solution (pH = 5.0) and heated to 70 °C while stirring. Then (VO)SO$_4$ · 2H$_2$O (0.23 g, 1.27 mmol) was slowly added in portions to the slightly yellowish solution of K$_{12}$[Sb$_2$W$_{22}$O$_{74}$(OH)$_2$]. The dark-brown reaction mixture resulted was stirred for 1 h at 70 °C, and then was allowed to cool at room temperature. The resulting pH value of the mixture was 4.5. After three days, crystals of K$_{10}$[(VO)$_2$Sb$_2$W$_{20}$O$_{70}$] · 20H$_2$O were obtained.

Synthesis of K$_{12}$[Bi$_2$W$_{22}$O$_{74}$(OH)$_2$] · 40H$_2$O (L$_2$)

A 30 g (90.95 mmol) amount of Na$_2$WO$_4$ · 2H$_2$O was dissolved in 40 mL of 4 M NaOAc/HOAc buffer solution. The mixture was heated to 100 °C and 2.52g (8.26 mmol) of BiONO$_3$ · H$_2$O was dissolved in 10 mL of concentrated HNO$_3$ (65%). After addition of 20 mL distilled water the bismuth-containing solution was added drop wise to the tungstate solution. The resulting mixture was heated for 2 h (95 °C). The potassium salt was precipitated by adding of grinded KCl solid (85 g, 114.09 mmol) with stirring. The desired product crystallized within 48 h as colorless plates.[16]

Synthesis of K$_{10}$[(VO)$_2$Bi$_2$W$_{20}$O$_{70}$] · 24H$_2$O (2)

The salt of $[(VO)_2Bi_2W_{20}O_{70}]^{10-}$ was prepared by the reaction of stoichiometric amounts of K$_{12}$[Bi$_2$W$_{22}$O$_{74}$(OH)$_2$] with the transition-metal salt (VO)SO$_4$ · 2H$_2$O. The potassium salt of $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$ (2 g, 0.29 mmol) prepared above was dissolved in 40 mL NaOAc/HOAc buffer solution (pH = 5.0) and heated to 70 °C while stirring. To this pale yellow solution of K$_{12}$[Bi$_2$W$_{22}$O$_{74}$(OH)$_2$] was given slowly (VO)SO$_4$ · 2H$_2$O (0.215 g, 1.18 mmol) in portions, leading to a deep-brown reaction mixture, with the final pH 4.3. After heating and stirring for 1 h at 70 °C, the mixture was allowed to cool to ambient temperature and then was filtered. After one week, the green-brown crystals of K$_{10}$[(VO)$_2$Bi$_2$W$_{20}$O$_{70}$] · 20H$_2$O complex were obtained. The translucent crystals were recrystallized from distilled water (pH = 4.5).

Physical-Chemical Measurements

The composition in vanadium, potassium and bismuth of each complex was determined by Atomic absorption.

The water content was estimated on the difference between the initial weight of the complex samples and their weight after they were heated at 120 °C for 30 minutes (Table 1). FT-IR spectra were recorded on a Jasco FT/IR 610 spectrometer in the 4000–400 cm^{-1} range, using KBr pellets.

Electronic spectra were performed in aqueous solutions having 10^{-5} –10^{-3} M concentrations, within a range

Table 1. Analytical data of the synthesized compounds.

Complex	Yield (g/%)	Color	Found (calc.) (%)				
			K	Sb/Bi	W	V	H_2O
1	2.56 / 70	yellow-brown	6.57 (6.48)	4.08 (4.12)	(62.24) 62.10	1.71 (1.60)	6.07 (6.23)
2	2.40 / 74	green-brown	6.31 (6.24)	6.77 (6.84)	59.60 (59.81)	1.65 (1.60)	(7.10)

of λ = 190–1000 nm on an ATI UNICAM-UV-Visible spectrophotometer with Vision Software V 3.20.
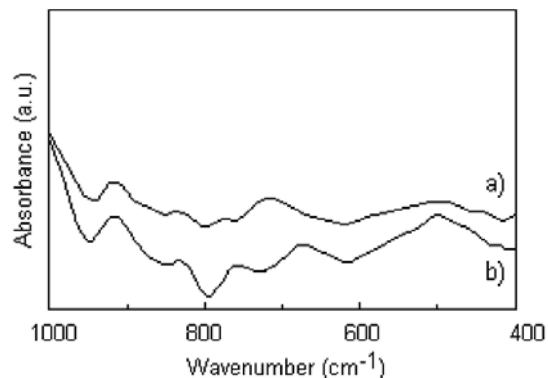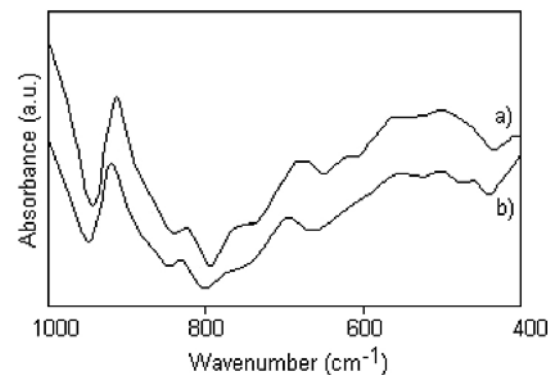
EPR spectra on powdered solids were recorded at room temperature at *ca.* 9.6 GHz (X band) using a Bruker ESP 380 spectrometer.

3. Results and Discussion

3. 1. FT-IR spectra

Some information about the coordination of the vanadium ions to the trilacunary POM units and the bonds strength were obtained by comparing the FT–IR spectra of the metallic complexes **1** and **2** and the corresponding ligand. The characteristic bands of the ligand and complexes are summarized in Table 2 and the main regions of the FT–IR spectra (400–1000 cm^{-1}) are given in Fig. 2 and Fig. 3.

The stretching vibration of the terminal W=O$_t$ bonds is shifted (with 8 cm^{-1} for **1** and 22 cm^{-1} for **2**) towards higher wave numbers in the FT-IR spectra of the complexes (Table 2), which indicates the involving of the terminal oxygen atoms in the coordination to the vanadium ions. The ν_{as}(W=O$_t$) vibration band is broader in the complexes spectra than the corresponding band in the ligand spectra because of its superposition with the stretching vibration ν_{as}(V=O).[17] The equivalence of the V=O groups in

Fig. 2 FT-IR spectra of the **L$_1$** ligand (a) and complex **1** (b).

Fig. 3 FT-IR spectra of the **L$_2$** ligand (a) and complex **2** (b).

Table 2. Some FT-IR bands (cm^{-1}) of the ligands (**L$_1$**, **L$_2$**) and (VO)^{II}–POM compounds (**1**, **2**).[a, b]

Band	**L$_1$**	**L$_2$**	**1**	**2**
ν_{as}(OH)	3332 s, b	3423 m, b	3427 s, b 3235 m, sh 3050 w, sh	3420 m, b 3242 m, sh
δ(HOH)	1619 w	1620 w, b	1617 w	1623 w, b
δ(OH)	1374	1384		
ν_{as}(W=Ot)	939 s	948 s	947 s	970 s
ν_{as}(X–O$_i$)	850 s	848 s	849 s	849 s
ν_{as}(W–O$_{c,e}$–W)	798 vs 761 s	794 vs 726 s, b	797 vs 750 s	792 vs 756 s, b
ν_s(W–O$_b$–W)	618 m, b	613 m, b	681 m, b	602 m, b

[a] O$_i$ is the oxygen which links the As and W atoms, O$_{c,e}$ connect corner and edge-sharing octahedral, respectively, O$_t$ is a terminal oxygen
[b] w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad.

the both complexes makes the corresponding vibration bands to be broad and unsplitted.

The bicentric X–O$_i$ bond is not shifted in complexes spectra compared to the ligands spectra due to their non-involving into the coordination of V^{IV} ions by the ligand. The vibration bands for the tricentric W–O$_c$–W bonds of the corner-sharing WO$_6$ octahedra observed in the FT-IR spectra of the complexes are non shifted comparing with the ligands. This is due to their non-involving into the coordination of the V^{IV} ions by O$_i$ atoms. The tricentric W–O$_e$–W bonds of the edge-sharing WO$_6$ octahedra have different stretching vibrations in both complexes. The v_{as}(W–O$_e$–W) vibration is blue shifted with 30 cm^{-1} in complex **2** FT-IR spectrum comparing to the ligand spectrum, but red shifted with 11 cm^{-1} in 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 v_{as}(W–O$_e$–W) frequency in complex **1** indicates the stretching of these bonds after the metallic ion complexation.[18] The increase of this frequency in complex **2** is in agreement with the shortening of these bonds after the complexation of the V^{IV} ions by the ligand.[17] The v_s(W–O$_e$–W) vibration is blue shifted with 63 cm^{-1} in complex **1** FT-IR spectrum comparing to the ligand spectrum, but red shifted with 11 cm^{-1} and blue shifted with 33 cm^{-1}, respectively, in complex **2** FT-IR spectrum. In addition, the FT-IR spectrum of complex **2** contains two W–O$_e$–W tricentric bands while the ligand spectrum contains a single band. This suggests the presence in the complexes of two nonequivalent W–O$_c$–W bonds.[19]

The W–O$_i$ bonds, where O$_i$ connects the tungsten with the heteroatom, present a single vibration in both ligands and complexes spectra (Table 2).

There is no evidence about the involving of these bonds in coordination process at the vanadium ions.[20] ŠRTF bookmark start: ćOLE_LINK1The shift of v_{as}(Bi–O$_{b,c}$–W), v_s(W–O$_b$–W), v_{as}(W–O$_c$–W) bands in the complex **1** comparative to the ligand **L$_1$** is due to the substitution of the lateral WO$_6$ octahedra by the (VO)O$_4$ square pyramid and the coordination of (VO)^{II} ions at O$_{b,c}$ type oxygens.[7] The FT–IR bands are broader in the complex, a part of them being overlapped. The v_{as}(W=O$_d$) frequency is unchanged by the substitution of two tungsten ions by two vanadyl ions, which is a sign of the structural stability of the β-B-BiW$_9$O$_{33}$ units.

The local symmetries around the (VO)^{II} ions in both (VO)^{II}–POM complexes are distorted C$_{4v}$ ((VO)O$_4$ local unit).

3. 2. Electronic Spectra

The UV electronic spectra of the (VO)^{II}–POM complexes and the two ligands **L$_1$** and **L$_2$** are similar (Fig. 4, Table 3). Each spectrum presents two bands assigned to ligand to metal charge transfer p$_\pi \to$ d$_\pi$ transitions in the W=O$_t$ bonds (at high wavenumbers) and the electron transition d$_\pi \to$ p$_\pi \to$ d$_\pi$ between the energetic levels of the tricentric bonds W–O$_b$–W (at low wave numbers).[12]
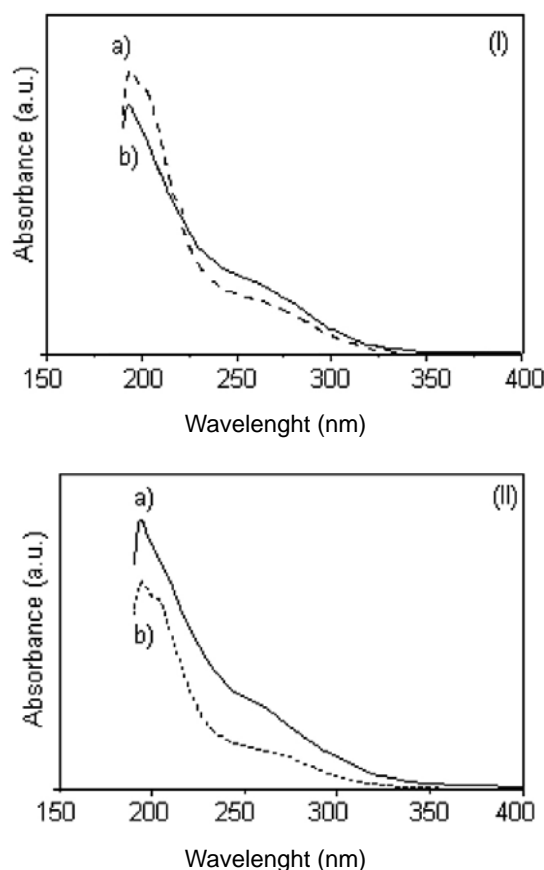

Fig. 4 UV spectra of synthetized ligands and complexes obtained in 5 · 10^{-5} mol l^{-1} aqueous solutions: ligand **L$_1$** (a) and complex **1** (b) (I); ligand **L$_2$** (a) and complex **2** (b), (II).

Table 3. UV spectral features (cm^{-1}/nm) of the(VO)^{II}–POM compounds and corresponding ligands.

p$_\pi \to$ d$_\pi$ (W=O$_t$)	52631/190	51280/195	54054/185	52631/190
Band cm^{-1}/nm	**L$_1$**	**L$_2$**	**1**	**2**
d$_\pi \to$ p$_\pi \to$ d$_\pi$ (W O$_b$ W)	37735/265 (40000/250 sh – (35714/280 sh)	37037/270 (39215/255 sh – 35087/285 sh)	37037/270 (40816/245 sh – 33898/295 sh)	36363/275 (40000/250 sh – 33333/300 sh)

The shifts of the maximum of the bands for the complex comparative to the ligand are due to the distortions introduced by the (VO)^{II} ions coordination to their neighboring WO_6 octahedra. The bicentric $W=O_t$ band is weakly shifted for complexes comparative to ligands. The band at lower wavelength for the $p_\pi(O_t) \rightarrow d_{\pi*}(W)$ transitions[21] appears at approximate the same wavelength (≈ 200 nm) in ligands spectra as well as in complexes spectra. The charge transfer transition is situated at ≈ 190 nm in L_1 ligand spectrum, shifted towards higher energies in complex **1** (at ≈ 185 nm), and is situated at ≈ 195 nm in L_2 ligand spectrum, shifted towards higher energies in complex **2** (at ≈ 190 nm) (Fig. 4).
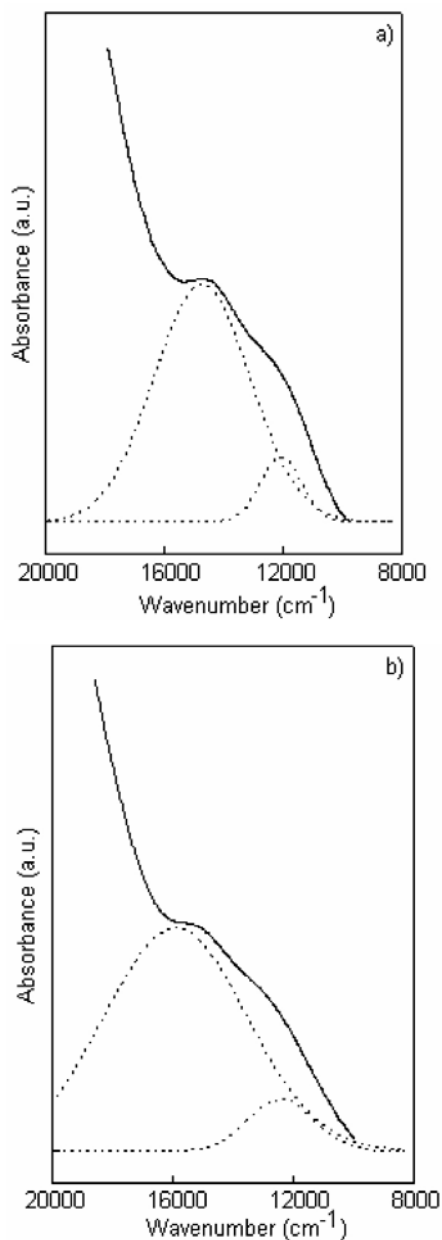

Fig. 5. Visible spectra of the complex 1 (a) and 2 (b), performed in $5 \cdot 10^{-3}$ mol l^{-1} aqueous solutions. The Gaussian components are represented with dashed lines.

The tricentric charge transfer band $d_\pi \rightarrow p_\pi \rightarrow d_\pi$ presents two shoulders for the (VO)^{II}–POM complexes and for the ligands. These bands are shifted in complexes towards lower energies comparative to the ligands because of the weakness of $W–O_b–W$ bonds after the (VO)^{II} complexation.

The visible electronic spectra of both complexes (Fig. 5) 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.[22]

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 complex **1** and at 12410 cm^{-1} and 15915 cm^{-1} for 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.[23] The higher energies for 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 -bondings, respectively.

3. 3. EPR spectra

The axial powder EPR spectra of both complexes were simulated by considering (VO)^{II} ions noninteracting (Fig. 6).
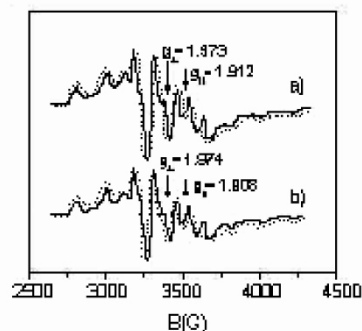

Fig. 6. Experimental (normal line) and simulated (dashed line) EPR spectra of the powder 1 (a) and 2 (b) complexes, at room temperature.

Powder EPR spectra of the $K_{10}[(V^{IV}O)_2X_2W_{20}O_{70}] \cdot xH_2O$ complexes (X=Sb^{III}, Bi^{III}), obtained in the X band at room temperature, correspond to the V^{IV} ions from the vanadyl groups of each molecule. The obtained spectra contain eight components, both in the perpendicular and in the parallel bands due to the hyperfine coupling of the spin of one unpaired electron with the nuclear spin of the ^{51}V isotope (I=7/2). The spectra can be described by an axial spin Hamiltonian characteristic for S=1/2 system with C_{4v} local symmetry:[24]

$$H = \mu_B[g_{II}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{II}S_zI_z + A_{\perp}(S_xI_x + S_yI_y)$$

where g_{II}, $g_{\perp t}$ and A_{II}, $A_{\perp t}$ are the axial principal values of the **g** and hyperfine tensors respectively, μ_B is the Bohr magneton, B_x, B_y, B_z are the components of the applied. magnetic field in direction of the principal **g** axes, S_x, S_y, S_z and I_x, I_y, I_z are the components of the electronic and nuclear spin angular momentum operators, respectively.

The best fit of the EPR spectra was made considering the parameters: $g_{\perp t} = 1.973$, $g_{II} = 1.912$, $A_{\perp t} = 69.5$ G, $A_{II} = 201.6$ G for complex **1** and $g_{II} = 1.908$, $g_{\perp t} = 1.974$, $A_{II} = 202.1$ G, $A_{\perp t} = 71.6$ G for complex **2**. These values suggest the equivalence of the two paramagnetic V^{IV} ions in each $K_{10}[(V^{IV}O)_2X_2W_{20}O_{70}] \cdot xH_2O$ units.

4. Conclusions

Two new polyoxometalate complexes of $[(VO)_2X_2W_{20}O_{70}]^{10-}$, $X=Sb^{III}$, Bi^{III}, were synthesized and investigated by means of elemental analysis, thermogravimetric, and spectroscopic methods (FT-IR, UV–VIS, EPR).

FT-IR data indicate the coordination of each vanadyl ion to oxygen atoms from corner-sharing and edge sharing octahedra. The UV spectra show that in the studied compounds, trilacunary Keggin anion plays the ligand role, as well as the secondary heteroatoms are the vanadyl cations. Visible electronic spectra indicate the penta-coordination in square-pyramidal environment of the vanadyl ions (C_{4v} symmetry with a d_{xy} orbital as ground state) in the investigated complexes. EPR parameters confirm the axial symmetry and noninteracting $(VO)^{II}$ ions.

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Povzetek

Pripravili smo kompleksa s sendvično strukturo $K_{12}[(VO)_2Sb_2W_{20}O_{70}]$ $31H_2O$ (**1**) in $K_{11}[(VO)_2Bi_2W_{20}O_{70}]$ $21H_2O$ (**2**) in jih preiskali s elementno analizo, termogravimetrijo in spektroskopijo (FT-IR, UV–VIS in EPR). Vrsto koordinacijo na vanadijev ion smo študirali s primerjavo FT-IR spektrov **1** in **2** s spektri ligandov $Na_9[BiW_9O_{33}]$ $14H_2O$ in $K_{12}[Bi_2W_{22}O_{74}(OH)_2]$ $40H_2O$. UV spektri kažejo premik trakov $p_{\pi}(O_{c,e}) \rightarrow d_{\pi*}(W)$ v kompleksih ≈ 245 nm v **1** in ≈ 250 nm v **2** proti proti nižjim vrednostim. Vidni spektri imajo trakove $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ in $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x2-y2})$ vanadilnega iona s C_{4v} točkovno simetrijo. EPR spektri pri sobni temperature kažejo na enojedrne oksovanadijeve spojine.