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Synthesis and physical-chemical study of sandwich-type heteropolyoxometalate with dinuclear vanadium clusters

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The sandwich-type $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot 20H_2O$ heteropolyoxotungstate was investigated by means of elemental analyses, thermogravimetric and spectroscopic (FT-IR, UV–VIS and EPR) methods. The analysis of vanadium ion coordination mode was made comparing the FT-IR spectrum of the complex with the $Na_9[BiW_9O_{33}]\cdot 14H_2O$ ligand. The stretching vibration of the terminal $W{=}O_t$ bonds is shifted with 8 cm^{-1} towards higher wave numbers in the FT-IR spectrum of the complex , which indicates the involving of the terminal oxygen atoms in the coordination to the vanadium ions. The $\nu_{as}(W–O_e–W)$ vibration is shifted with 11 cm^{-1} in complex FT-IR spectrum. This behavior arrises from different deformations induced by the vanadium ions coordination in the frame of the trilacunary ligand. The decrease of the $\nu_{as}(W–O_e–W)$ frequency in complex indicates the stretching of these bonds after the metallic ion complexation. The shift of $\nu_{as}(Bi–O_{b,c}–W)$, $\nu_s(W–O_b–W)$, $\nu_{as}(W–O_c–W)$ bands in the complex comparative to the ligand 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. 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 ≈ 245 cm^{-1} towards higher wavelength. Visible spectra contain the $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ transition bands for vanadyl ions in C_{4v} local symmetry, at 12040 cm^{-1} and respectively 14705 cm^{-1} for the complex. The powder EPR spectrum obtained in the X band at room temperature are typical for mononuclear oxovanadium species in an axial environment. The spectrum exhibits eight components both in the perpendicular and in the parallel bands ($g_\perp = 1.973$, $g_{II} = 1.912$, $A_\perp = 69.5$ G, $A_{II} = 201.6$ G).

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1. Introduction

A special class of heteropolyoxometalates (HPOM) substituted by early transition metals (3d) is the unsaturated trilacunary Keggin-type $[X^{n+}W_9O_{33}]^{(12-n)-}$ structure, where the heteroatom X is the Sb^{III} ions [1-2].The main characteristic of this ions is the presence of one pair of electrons, which prevents further condensation to a saturated Keggin structure [4-6]. 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} as subvalent heteroatom have been reported, the chemistry of heteropolyoxotungstates being a new, but expanding field of research.

In this work we investigate the new $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot 20H_2O$ sandwich-type complex 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} [8-9], related by a center of inversion and facing each other with their open sites. A belt of two vanadium ions connects the trilacunary anions [3, 10]. Formally, the *fac*-WO_3 groups have been exchanged for transition-metal ions with three aqua 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 $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 38H_2O$ (ligand)

The sodium salt of $[SbW_9O_{33}]^{9-}$ [1] (10 g, 3.49 mmol) and $Na_2WO_4\cdot 2H_2O$ (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 $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 38H_2O$ 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 $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot 20H_2O$ (complex)

The salt of $[(VO)_2Sb_2W_{20}O_{70}]^{10-}$ was prepared by the reaction of stoichiometric amounts of $K_{12}[Sb_2W_{22}O_{74}(OH)_2]$·with the transition-metal salt $(VO)SO_4\cdot 2H_2O$. The potassium salt of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (2 g, 0.3 mmol) prepared above was suspended in 40 mL NaOAc/HOAc buffer solution (pH = 5.0) and heated to 70°C while stirring. Then $(VO)SO_4\cdot 2H_2O$ (0.23 g, 1.27 mmol) was slowly added in portions to the slightly yellowish solution of $K_{12}[Sb_2W_{22}O_{74}(OH)_2]$. 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 $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot 20H_2O$ were obtained.

The translucent crystals were recrystallized from distilled water (pH = 4.5) (Table 1).

Table 1. Analytical data of the synthesized compounds.

Complex	Yield (g / %)	Color	Found (calc.) (%)				
			K	Sb	W	V	H_2O
1	2.56 / 70	yellow-brown	6.57 (6.48)	4.08 (4.12)	62.10 (62.24)	1.71 (1.60)	6.07 (6.23)

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 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 complex and the corresponding ligand (L = $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 38H_2O$).

The characteristic bands of the ligand and complex are summarized in Table 2 and the main regions of the FT–IR spectra (400 – 1000 cm^{-1}) are given in Fig 2.

The stretching vibration of the terminal W=O$_t$ bond is shifted (with 8 cm^{-1}) towards higher wave numbers in the FT-IR spectrum of the complex (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 complex spectrum than the corresponding band in the ligand spectrum because of its superposition with the stretching vibration ν_{as}(V=O) [11]. The equivalence of the V=O groups in the complex makes the corresponding vibration bands to be broad and unsplitted.

The bicentric X–O$_i$ bond is not shifted in complex spectrum compared to the ligand spectrum due to their non-involving into the coordination of V^{IV} ions by the ligand.

The vibration band for the tricentric W–O$_c$–W bond of the corner-sharing WO$_6$ octahedra observed in the FT-IR spectrum of the complex are non shifted comparing with the ligand. This is due to their non-involving into the coordination of the V^{IV} ions by O$_i$ atoms.

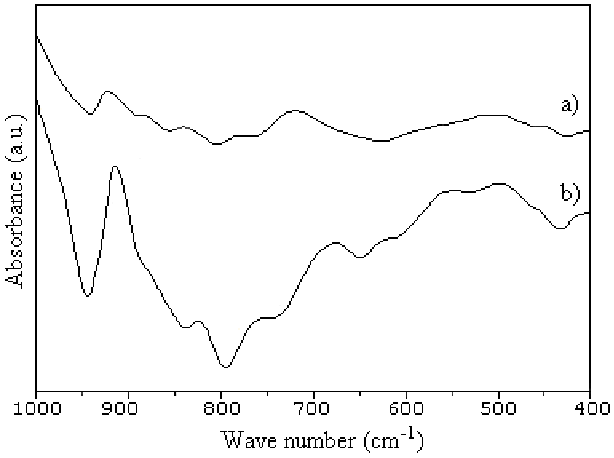

Fig. 2. FT-IR spectra of the (a) ligand and (b) complex Sb.

Table 2. Some FTIR bands (cm^{-1}) of the ligand and (VO)^{II}–POM compound.

Band	Sb_2W_{22}	Sb_2W_{20}
ν_{as}(OH)	3332 s, b	3427 s, b 3235 m, sh 3050 w, sh
δ(HOH) δ(OH)	1619 w 1374	1617 w
ν_{as}(W=O$_t$)	939 s	947 s
ν_{as}(X–O$_i$)	850 s	849 s
ν_{as}(W–O$_{c,e}$–W)	798 vs 761 s	797 vs 750 s
ν_s(W–O$_b$–W)	618 m, b	681 m, b

w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad.

The tricentric W–O$_e$–W bond of the edge-sharing WO$_6$ octahedra has different stretching vibration in the complex. The ν_{as}(W–O$_e$–W) vibration is red shifted with 11 cm^{-1} in complex FT-IR spectrum. This behavior arrises from different deformations induced by the vanadium ions coordination in the frame of the trilacunary ligand. The decrease of the ν_{as}(W–O$_e$–W) frequency in complex indicates the lengthening of this bond after the metallic ion complexation [12].

The ν_s(W–O$_e$–W) vibration is blue shifted with 63 cm^{-1} in complex FT-IR spectrum comparing to the ligand spectrum. This suggests the presence in the complexes of two nonequivalent W–O$_c$–W bonds [13].

The W–O$_i$ bonds, where O$_i$ connects the tungsten with the heteroatoms, present a single vibration in both ligand and complex spectra (Table 2). There is no evidence about the involving of these bonds in coordination process at the vanadium ions [14].

The shift of ν_{as}(Bi–O$_{b,c}$–W), ν_s(W–O$_b$–W), ν_{as}(W–O$_c$–W) bands in the complex comparative to the ligand 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 [4]. The FT–IR bands are broader in the complex, a part of them being overlapped. The ν_{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} symmetry ((VO)O$_4$ local unit).

3.2. Electronic spectra

The UV electronic spectra of the (VO)^{II}–POM complex and the ligand are similar (Fig. 3, Table 3). Each spectrum presents two bands assigned to ligand to metal charge transfer $p_\pi \rightarrow d_\pi$ transitions in the W=O$_t$ bonds (at high wavenumbers) and the electron transition $d_\pi \rightarrow p_\pi \rightarrow d_\pi$ between the energetic levels of the tricentric bonds W–O$_b$–W (at low wave numbers) [7].

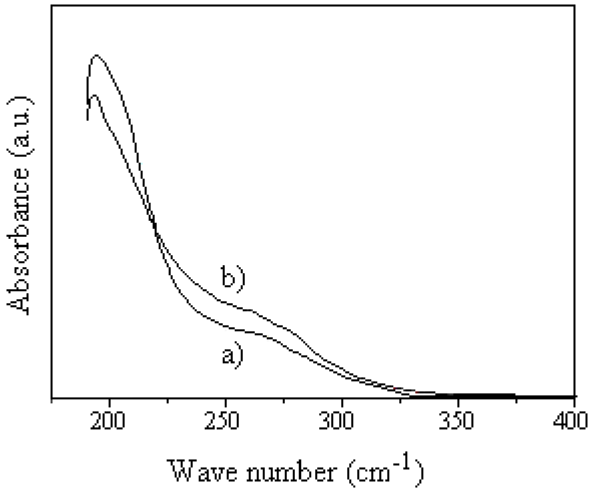

Fig. 3 UV spectra of synthetized (b) ligand and (a) complex obtained in 5×10^{-5} mol l^{-1} aqueous solutions.

Table 3. Uv spectral features (cm^{-1}/nm) of the(vo)^{ii}–pom compound and corresponding ligand.

Band cm^{-1}/nm	**Ligand**	**Complex**
$d_\pi \rightarrow p_\pi \rightarrow d_\pi$ (W–O$_b$–W)	37735/265 (40000/250 sh – 35714/280 sh)	37037/270 (40816/245 sh – 33898/295 sh)
$p_\pi \rightarrow d_\pi$ (W=O$_t$)	52631/190	54054/185

sh, shoulder

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 UV electronic spectra of the complex and ligand (Fig. 3) contain two 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 [15] appears at approximate the same wavelength (≈200 nm) in ligand spectrum as well as in complex spectrum. The charge transfer transition is situated at ≈ 190 nm in ligand spectrum, shifted towards higher energies in complex (at ≈ 185 nm) (Fig. 3).

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

The visible electronic spectrum of complex (Fig. 4) 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} → W^{VI} charge transfer transitions [16]. The Gaussian analyses of the spectrum lead to obtaining the position of the bands for V^{IV} ions d-d transitions. For complex appear two bands at 12040 cm^{-1} and 14705 cm^{-1}. The bands of complex are related to the $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ (I) and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_x2\ _{-\ y}2)$ (II) transitions in the Ballhausen and Gray molecular orbital theory for vanadyl ions in C_{4v} local symmetry [17].

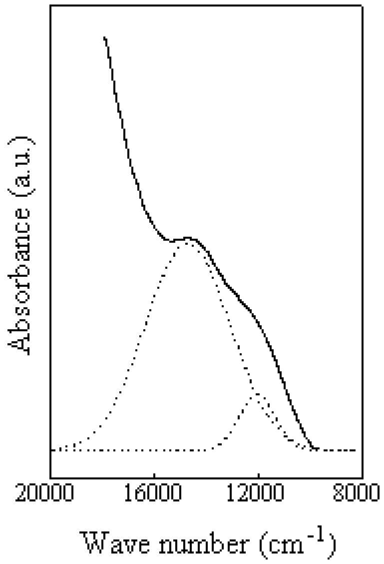

Fig. 4 Visible spectra of the complex performed in 5×10^{-3} mol l^{-1} aqueous solutions. The Gaussian components are represented with dashed lines.

3.3. EPR spectra

The axial powder EPR spectra of both complexes were simulated by considering $(VO)^{II}$ ions noninteracting and S = 1/2 ground state [3] (Fig. 5).

The compound derive from the $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot20H_2O$ anions in which two β-B-XW_9O_{33} units are connected by two WO_6 octahedra and two lateral $(VO)O_4$ groups.

Powder EPR spectrum of the $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot20H_2O$ complex obtained in the X band at room temperature, correspond to the V^{IV} ions from the vanadyl groups of each molecule. The obtained spectrum 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 spectrum can be described by an axial spin Hamiltonian characteristic for S = 1/2 system with C_{4v} local symmetry [18]:

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

where g_{II}, $g_\perp$ and A_{II}, $A_\perp$ 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.

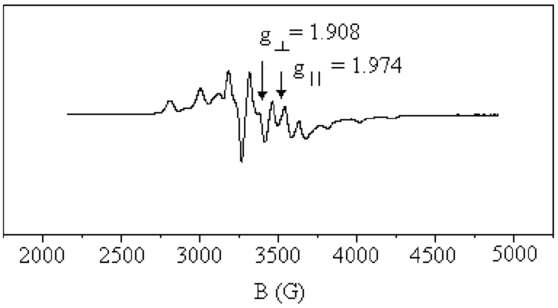

Fig. 5 Simulated EPR spectrum of the powder complex at room temperature.

The EPR parameters ($g_\perp$ = 1.973, g_{II} = 1.912, $A_\perp$ = 69.5 G, A_{II} = 201.6 G) suggests 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

The new polyoxometalate complex of $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot20H_2O$ was synthesized and investigated by means of elemental analysis, thermogravimetry, 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 complexes 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 (C4v symmetry with 2B2(dxy) ground state) in the investigated complexes. EPR parameters confirm the axial symmetry and noninteracting $(VO)^{II}$ ions.

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