

Spectroscopic study of dinuclear vanadium cluster encapsulated in sandwich-type heteropolyoxometalate

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The sandwich-type $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ heteropolyoxotungstate was investigated by means of elemental analyses, thermogravimetry and spectroscopic methods (FT-IR, UV-VIS and EPR). The analysis of the coordination mode of the vanadium ions was made by comparing the FT-IR spectrum of the complex those of the $K_{12}[Bi_2W_{22}O_{74}(OH)_2] \cdot 40H_2O$ ligand. FT-IR spectrum of the complex show the presence of the V=O bonds characterized by $\nu_{as}(V=O)$ vibrations. In the complex, the coordination of the vanadium shifts the $\nu_s(W-O_{c,e}-W)$ vibration bands. In UV spectrum, the charge transfer $p_{\pi}(O_{c,e}) \rightarrow d_{\pi}(W)$ band is shifted in complex compared to the ligand spectrum with $\approx 250 \text{ cm}^{-1}$ towards lower wave numbers. Visible spectrum of the complex contain at 12405 cm^{-1} and 15905 cm^{-1} 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. 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 ($g_{\parallel} = 1.908$, $g_{\perp} = 1.974$, $A_{\parallel} = 201.6 \text{ G}$, $A_{\perp} = 69.5 \text{ G}$).

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1. Introduction

The sandwich-type heteropolymetalates encapsulating clusters of early transition metals have received much attention both from applied and fundamental research perspectives. These complexes have the capacity to include more transition metals, which interact by means of dipolar or exchange coupling [1, 2]. This aspect recommends heteropolyoxometalates as potential hosts of high dimensional clusters [1, 3, 4, 5].

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 [6, 7]. The main characteristic of these ions is the presence of one pair of electrons, which prevents further condensation to a saturated Keggin structure [4]. However, transition metal ions could link the lacunary units, resulting a sandwich-type structure.

In this work we investigate the new $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ 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 (Fig. 1). [10, 11]

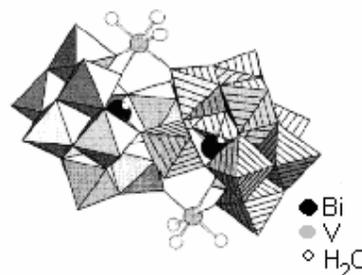


Fig. 1. The structure of $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ complex. (The shaded and grey units are $\{B-\beta-BiW_9\}$ fragments and $\{WO_6\}$ bond octahedral, the Bi centres are represented as black spheres, the V centres are represented as large size grey spheres and the water molecules are represented as small white spheres).

2. Experimental section

All chemicals were of reagent grade and used without further purification. The $[BiW_9O_{33}]^{9-}$ unit have been synthesized as previously described [8].

Synthesis of $K_{12}[Bi_2W_{22}O_{74}(OH)_2] \cdot 40H_2O$ (L)

A 30 g (90.95 mmol) amount of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 40 mL of 4 M NaOAc/HOAc buffer solution. The mixture was heated to $100^\circ C$ and 2.52g (8.26 mmol) of $BiONO_3 \cdot H_2O$ 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 [9].

Synthesis of $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ (1)

The salt of $[(VO)_2Bi_2W_{20}O_{70}]^{10-}$ was prepared by the reaction of stoichiometric amounts of $K_{12}[Bi_2W_{22}O_{74}(OH)_2]$ with the transition-metal salt $(VO)SO_4 \cdot 2H_2O$. 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 $K_{12}[Bi_2W_{22}O_{74}(OH)_2]$ was given slowly $(VO)SO_4 \cdot 2H_2O$ (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 $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 20H_2O$ 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.

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 $\lambda = 190$ – 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 with the corresponding ligand. The main regions of the FT-IR spectra (400 – 1000 cm^{-1}) are given in Fig. 2 and some of the bands and their assignments are shown in Table 1.

Table 1. Some FTIR bands (cm^{-1}) of the ligand **L** and **1** compound.

Band	L	1
$\nu_{as}(W=O_i)$	948 s	970 s
$\nu_{as}(X-O_i)$	848 s	849 s
$\nu_{as}(W-O_{e,e}-W)$	794 vs 726 s, b	792 vs 756 s, b
$\nu_s(W-O_b-W)$	613 m, b	646 m, b 602 m, b

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

The stretching vibration of the terminal $W=O_t$ bonds is shifted (with 22 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 $\nu_{as}(W=O_t)$ vibration band is broader in the complex spectrum than the corresponding band in the ligand spectrum because of its superposition with the stretching vibration $\nu_{as}(V=O)$ [12]. The equivalence of the $V=O$ groups in the complex makes the corresponding vibration bands to be broad and unsplit.

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 bands for the tricentric $W-O_e-W$ bonds 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.

The tricentric $W-O_e-W$ bonds of the edge-sharing WO_6 octahedra have different stretching vibrations in the complex. The $\nu_{as}(W-O_e-W)$ vibration is blue shifted with 30 cm^{-1} in complex FT-IR spectrum comparing to the ligand spectrum. This behavior arises from different deformations induced by the vanadium ions coordination in the frame of the trilacunary ligand. The increase of the $\nu_{as}(W-O_e-W)$ frequency in complex is in agreement with the shortening of these bonds after the complexation of the V^{IV} ions by the ligand [13].

The $\nu_s(W-O_e-W)$ vibration is red shifted with 11 cm^{-1} and blue shifted with 33 cm^{-1} in complex FT-IR spectrum comparing to the ligand spectrum. In addition, the FT-IR spectrum of complex 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 $W-O_e-W$ bonds [14].

The $W-O_i$ bonds, where O_i connects the tungsten with the heteroatoms, present a single vibration in the ligand and complex spectrum. There is no evidence about the involving of these bonds in coordination process at the vanadium ions [15].

The local symmetries around the vanadium ions in the $(VO)^{II}$ -POM complex are distorted C_{4v} symmetry ($(VO)O_4$ local unit).

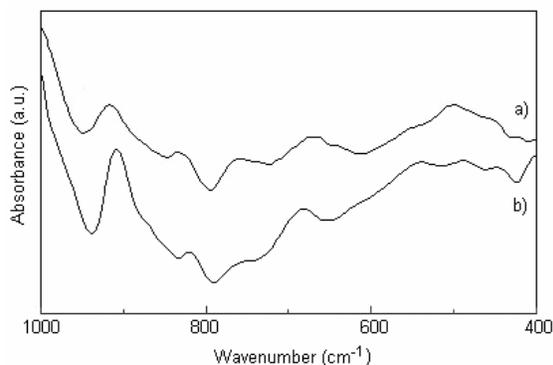


Fig. 2. FT-IR spectra of the ligand (a) and complex (b).

3.2. Electronic spectra

The UV electronic spectra of the $(VO)^{II}$ -POM complex and the ligand **L** are similar (Fig. 3).

The 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) [16].

The band at lower wavelength for the $p_{\pi}(O_t) \rightarrow d_{\pi}^*(W)$ transitions [17] appears at approximate the same wavelength (≈ 200 nm) in ligand spectrum as well as in complex spectrum. The charge transfer transition is situated at ≈ 195 nm in ligand spectrum, shifted towards higher energies in complex (at ≈ 190 nm).

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 the 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 $V^{IV} \rightarrow W^{VI}$ charge transfer transitions [18]. 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 12410 cm^{-1} and 15915 cm^{-1} attributed 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, respectively, in the Ballhausen and Gray molecular orbital theory for vanadyl ions in C_{4v} local symmetry [19]. The higher energies for complex 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.

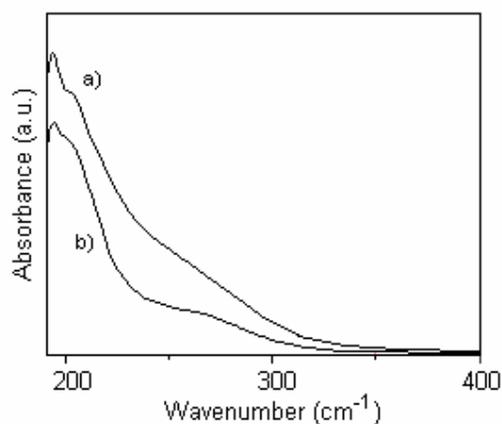


Fig. 3. UV spectra of synthesized ligand (a) and complex (b) obtained in $5 \times 10^{-5}\text{ mol l}^{-1}$ aqueous solutions.

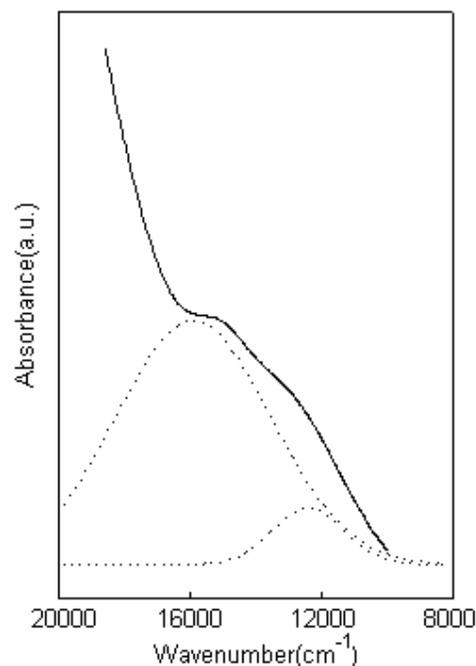


Fig. 4. Visible spectra of the complex performed in $5 \times 10^{-3}\text{ mol l}^{-1}$ aqueous solutions. The Gaussian components are represented with dashed lines.

3.3. EPR spectra

The axial powder EPR spectrum of the complex was simulated by considering $(VO)^{II}$ ions noninteracting and $S = 1/2$ ground state [4] (Fig. 5).

Powder EPR spectrum of the $K_{10}[(V^{IV}O)_2Bi_2W_{20}O_{70}] \cdot xH_2O$ 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 [20]:

$$H = \mu_B [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

where g_{\parallel} , g_{\perp} and A_{\parallel} , 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.

The best fitting simulated EPR parameters ($g_{\parallel} = 1.908$, $g_{\perp} = 1.974$, $A_{\parallel} = 201.6$ G, $A_{\perp} = 69.5$ G) suggests the equivalence of the two paramagnetic V^{IV} ions in $K_{10}[(V^{IV}O)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ units.

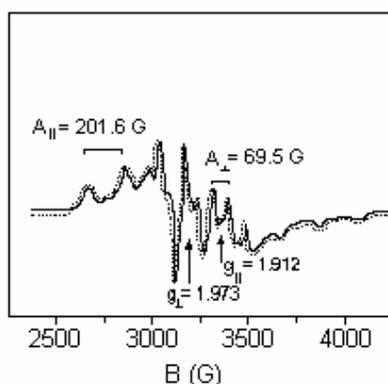


Fig. 5. Experimental (normal line) and simulated (dashed line) EPR spectrum of the powder complex, at room temperature.

4. Conclusions

The polyoxometalate complex of $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ 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 spectrum show that in the studied complex trlacunary Keggin anion plays the ligand role, as well as the secondary heteroatoms are the vanadyl cations. Visible electronic spectrum indicates 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 complex. EPR parameters confirm the axial symmetry and noninteracting $(VO)^{II}$ ions.

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