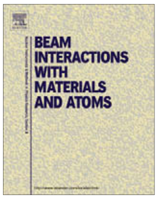
Nuclear Instruments and Methods in Physics Research B 267 (2009) 422–425

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Structural investigations of sandwich-type heteropolyoxometalate with dinuclear vanadium cluster

O. Baban [a], I. Hauer [b], D. Rusu [c], M. Rusu [a], N.L. Mogonea [b], L. David [b,*]

[a] Faculty of Chemistry, Babes-Bolyai University, 400028 Cluj-Napoca, Romania
[b] Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania
[c] Faculty of Pharmacy, Iuliu Hatieganu University, 400032 Cluj-Napoca, Romania

ARTICLE INFO

Available online 11 November 2008

PACS:
33.20.Ea
33.20.Kf
33.20.Lg
33.35+r

Keywords:
Heteropolyoxometalate
FT-IR
UV–vis
EPR

ABSTRACT

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 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 involvement of the terminal oxygen atoms in the coordination to the vanadium ions. The UV electronic spectra of the ligand and complex spectrum presents two bands assigned to ligand to metal charge transfer $p_\pi \rightarrow d_\pi$ transitions in the $W{=}O_t$ bonds and the electron transition $d_\pi \rightarrow p_\pi \rightarrow d_\pi$ between the energetic levels of the tricentric bonds $W–O_b–W$. The powder EPR spectrum obtained at room temperature is typical for mononuclear oxovanadium species in an axial environment. The spectrum exhibits eight components, both in perpendicular and parallel bands due to the hyperfine coupling of the spin of one unpaired electron with the nuclear spin of the ^{51}V isotope ($g_\perp = 1.908$, $g_{II} = 1.974$, $A_\perp = 69$ G, $A_{II} = 201$ G).

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 [3–6].

In this paper, we have investigated 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} [7–9], related by a center of inversion and facing each other with their open sites (Fig. 1). 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

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

2.1. Synthesis of $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 38H_2O$ (**L**)

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 recrystallization 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.

2.2. Synthesis of $K_{10}[(VO)_2Sb_2W_{20}O_{70}]\cdot 20H_2O$

The salt of $[(VO)_2Sb_2W_{20}O_{70}]^{10-}$ was prepared by the reaction of stoichiometric amounts of $K_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot$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

---

* Corresponding author.
E-mail address: leodavid@phys.ubbcluj.ro (L. David).

0168-583X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2008.10.085

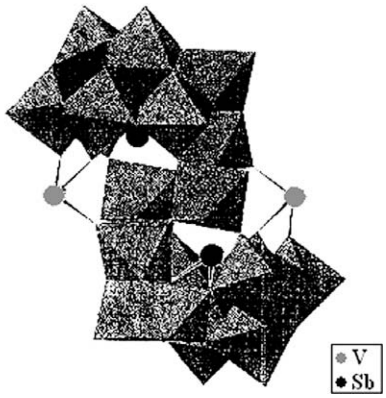


Fig. 1. Polyhedral plot of $[(VO)_2Sb_2W_{20}O_{70}]^{10-}$.

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).

The analytical data for the synthesized complex are: yield 2.56/70 g/%, elemental analysis results: found/(calculated): %K 6.57/(6.48), %Sb: 4.08/(4.12), %W: 62.10/(62.24), %V: 1.71/(1.60), $\%H_2O$: 6.07/(6.23).

2.3. 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 min. 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 9.6 GHz (X band) using a Bruker ESP 380 spectrometer.

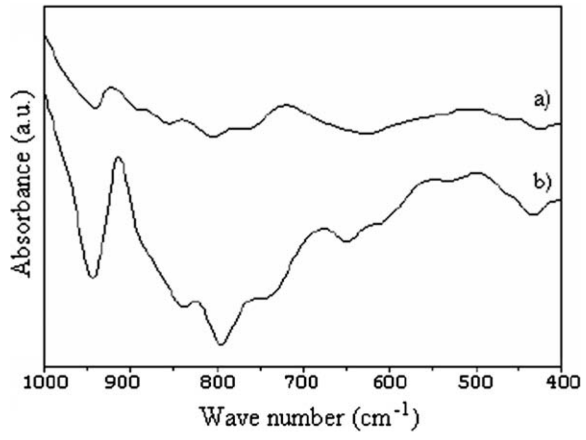


Fig. 2. FT-IR spectra of the ligand (a) and complex (b).

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

Band	L	$(VO)^{II}$–POM
$\nu_{as}(OH)$	3332 s, b	3427 s, b 3235 m, sh 3050 w, sh
$\delta(HOH)$	1619 w	1617 w
$\delta(OH)$	1374	
$\nu_{as}(W{=}O_t)$	939 s	947 s
$\nu_{as}(XO_i)$	850 s	849 s
$\nu_{as}(WO_{c,e}W)$	798 vs 761 s	797 vs 750 s
$\nu_s(WO_bW)$	618 m, b	681 m, b

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

3. Results and discussion

3.1. Fourier transform infrared spectra (FT-IR)

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 (Fig. 2) of the metallic complex and the corresponding ligand (**L** = $K_{12}\ [Sb_2W_{22}O_{74}(OH)_2]{\cdot}38H_2O$).

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 1), 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 $\nu_{as}(V{=}O)$ [11]. The equivalence of the V=O groups in the complex makes the corresponding vibration bands to be broad and unsplitted.

The tricentric WO_eW bond of the edge-sharing WO_6 octahedra has different stretching vibration in the complex. The $\nu_{as}(WO_eW)$ vibration is red shifted with 11 cm^{-1} in complex FT-IR spectrum. This behavior arises from different deformations induced by the vanadium ions coordination in the frame of the trilacunary ligand. The decrease of the $\nu_{as}(WO_eW)$ frequency in complex indicates the lengthening of this bond after the metallic ion complexation [12].

The $\nu_s(WO_eW)$ 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 WO_cW bonds [13]. The WO_i bonds, where O_i connects the tungsten with the heteroatoms, present a single vibration in both ligand and complex spectra (Table 1). There is no evidence about the involving of these bonds in coordination process at the vanadium ions [14].

The shift of $\nu_{as}(BiO_{b,c}W)$, $\nu_s(WO_bW)$, $\nu_{as}(WO_cW)$ 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 $\nu_{as}(W{=}O_d)$ 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_9O_{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 ultraviolet (UV) electronic spectra of the $(VO)^{II}$POM complex and the ligand are similar (Figs. 3 and 4). 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 wave numbers) and the electron transition $d_\pi \rightarrow p_\pi \rightarrow d_\pi$ between the energetic levels of the tricentric bonds WO_bW (at low wave numbers) [7].