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New heteropolyoxometalates with Keggin and Dawson structure and with mixed addend atoms

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The sandwich-type $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ (**1**) and $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$ (**2**) complexes were prepared and investigated by means of elemental analysis and spectroscopic methods (FT-IR, UV, VIS, EPR). The analysis of the coordination mode of the vanadium ions was made by comparing the FT-IR spectra of the complexes **1** and **2** with those of the ligands $K_7[SiMo_2W_9O_{39}]\cdot 14H_2O$ and $K_{12}[Si_2MoW_{16}O_{61}]\cdot 19H_2O$ respectively. The stretching vibration of the terminal $W{=}O_t$ bonds is shifted towards higher wavenumbers in the FTIR spectra of the complexes, which indicates the involving of the terminal oxygen from $W{=}O_t$ bonds in the coordination to the vanadium ions. The opposite shift of $\nu_{as}(W\text{-}O_e\text{-}W)$ and $\nu_{as}(W\text{-}O_c\text{-}W)$ vibrations bands shows the co-ordination of each vanadium ion at oxygen atoms from the belt region. The UV electronic spectra of the ligands and complexes exhibit two strong and broad change transfer bands at ~200 nm and ~250 nm, assigned to $W\text{-}O_t$ (ν_1) and $W\text{-}O_b\text{-}W$ (ν_2) transitions respectively. The visible electronic spectra in aqueous solution are typically for V^{IV} ions in O_h distorted local symmetry. The powder EPR spectra of both complexes are axial and exhibits eight hyperfine components both in the perpendicular and the parallel bands, due to the hyperfine coupling of the unpaired electron.

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Keywords: Heteropolyoxometolates, Keggin structure, Dawson structure

1. Introduction

Heteropolyoxometalates (HPOM) are intensely studied for their use in catalysis, biology and materials science. When these polyanions contain vanadium and molybdenum atoms near the tungsten and oxygen atoms, they exhibit important catalytic activities for redox reactions [1].

Heteropolyoxometalates (HPOM) with mixed addend atoms like vanadium, molybdenum or tungsten are also very interesting from structural point of view [2, 3]. The proximity of the easier vanadium and molybdenum ions into the structure [2], the presence of mixed valence anions, the unpaired electron delocalization into the HPOM [3,4] or contrary the presence of trapped electrons on different ions [5-6] are some structural features leading to different spectroscopic properties and applications of these compounds.

Here are reported some spectroscopic and magnetic investigations on $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ heteropolyoxometalate (V^{IV}–HPOM) and its monoprotonated form**.** This complex presents one α-Keggin structure [7] (Fig. 1) and it derives from the monovacant α-A-$[SiMo_2W_9O_{39}]^{7-}$ anion to which one vanadium ion is added [8].

Another compound that was investigated is the $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$ complex. This complex has an α-Dawson–Wells structure [1, 7] with one tungsten atom substituted by one easier molybdenum atom and another tungsten atom replaced by one vanadium ion (Fig. 2). The two silicon atoms are tetrahedrally coordinated in the center of the investigated heteropolyoxometalate complex.

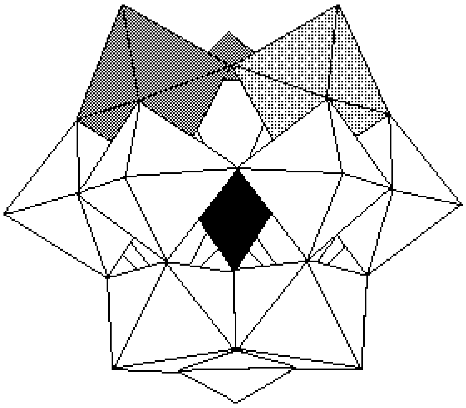

Fig. 1. The structure of $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ heteropolyoxometalate. (Shaded octahedra in the "cap" position represent MoO_6 sites. Pointed octahedrum is the VO_6 unit. The empty polyhedra are WO_6 units and the full central tetrahedron is SiO_4).

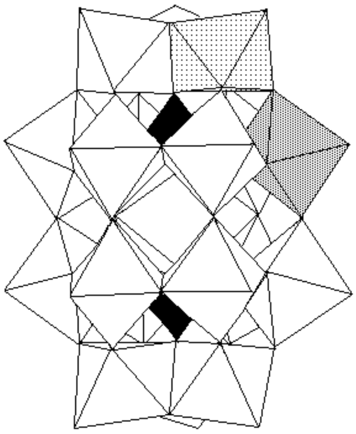

Fig. 2. The crystalline structure of the $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$ heteropolyoxometalate (Shaded octahedron in the "belt" position represents VO_6 site. Pointed octahedron in the "cap" position represents the MoO_6 site).

2. Experimental section

Synthesis of $K_7[SiMo_2W_9O_{39}]\cdot 14H_2O$ (L_1)

$Na_2MoO_4\cdot 2H_2O$ (3.70g, 15.28 mmol) was suspended in hot water (30 ml) and Na_2WO_4 (5g, 15.15 mmol) and Na_2SiO_3 (1,85g, 15.16 mmol) was successively added with magnetic stirring. The solution was heated and at reflux for 3.5 h (pH recorded 4.5). KCl was then added to the hot solution and the solution stirred for the further 10 min. The white powder was collected by vacuum filtration and air dried.

Synthesis of $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ (1)

$VOSO_4\cdot 2H_2O$ (0.36g, 2.2 mmol) was suspended in 23 ml H_2O and $K_7[SiMo_2W_9O_{39}]\cdot 14H_2O$ (6.36g, 2.0 mmol) was added with magnetic stirring. The solution was stirred 30 min. KCl (0.75g, 10.06 mmol) was added and the solution was stirred again for the further 10 min. The resulting solution was made to settle in a refrigerator until the black-blue crystals formed. They were collected and recrystallized from warm water.

Synthesis of $K_{12}[Si_2MoW_{16}O_{61}]\cdot 19H_2O$ (L_2)

$Na_2WO_4\cdot 2H_2O$ (5.0g, 15.15 mmol) was suspended in hot water (30 ml) and Na_2SiO_3 (1.0g, 8.1 mmol) and H_2SO_4 (pH = 4.0) was successively added with magnetic stirring. The yellow solution was heated and at reflux for 5 h and after that some HNO_3 was added to eliminate some products of reduction which have blue color. KCl was then added stirred for the further 10 min. The white powder $K_8[Si_2W_{18}O_{62}]\cdot aq$ was collected by vacuum filtration and air dried. To substitued one W atom with an Mo atom, $K_8[Si_2W_{18}O_{62}]\cdot aq$ (4g, 0.85 mmol) was suspended in a $Na_2MoO_4\cdot 2H_2O$, 2N solution and 200 ml HCl 6N was added. The solution was heated and at reflux for 5 h. KCl was then added to the hot solution and a white powder $K_8[Si_2MoW_{17}O_{62}]$ precipitated. Finally, $K_8[Si_2MoW_{17}O_{62}]$ (4g, 0.85 mmol) was suspended in 15.5 ml water and 200ml $KHCO_3$ solution 1N was added to pH = 6.0 – 6.5. KCl was then added to the solution. The white powder $K_{12}[Si_2MoW_{16}O_{61}]\cdot 19H_2O$ was collected by vacuum filtration and air dried.

Synthesis of $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$

$VOSO_4\cdot 2H_2O$ (0.1g, 0.61 mmol) was suspended in 3 ml H_2O and $K_{12}[Si_2MoW_{16}O_{61}]\cdot 19H_2O$ (1.70g, 0.33 mmol) was added with magnetic stirring. The solution was stirred 30 min. KCl (0.4g, 5.3 mmol) was added and the solution was stirred again for the further 10 min. The resulting solution was made to settle in a refrigerator until the black-blue crystals formed. They were collected and recrystallized from warm water.

3. Results and discussion

3.1 Chemical analysis

The reaction of VO^{2+} with **$SiMo_2W_9$** and **Si_2MoW_{16}** in water according to the eqn. (1 and 2), followed by isolation as potassium salts and recrystallization from hot water, results in good yields of the **(1)** and **(2)** complexes.

$$VO^{2+} + [SiMo_2W_9O_{39}]^{8-} \rightarrow [(VO)SiMo_2W_9O_{39}]^{6-} \quad (1)$$

$$VO^{2+} + [Si_2MoW_{16}O_{61}]^{12-} \rightarrow [(VO)Si_2MoW_{16}O_{61}]^{10-} \quad (2)$$

The study of the new vanadyl tungstosilicates thermal behavior, which consist of heating of the samples at 120°C for 30 minutes, reveals that both of the complexes contain 14 and respectively 18 crystallization water molecules (Table 1).

Table 1. Analitycal data of the synthesized compounds.

Compound	K %		V %		Mo %		W %		H_2O %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	7.68	7.54	1.66	1.56	6.28	6.23	54.20	54.00	8.26	8.30
2	8.14	8.08	1.06	1.00	1.99	1.92	61.17	61.15	6.75	6.82

3.2 FT-IR spectra

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 ligands. Fig. 3-4 presents the main part of the FTIR spectra and some of the bands and their assignments are shown in Table 2.

The stretching vibration of the terminal W=O_t bonds is shifted (with 21 cm^{-1} for **1** and 40 cm^{-1} for **2**) towards higher wavenumbers in the FTIR spectra of the complexes (Table 2), which indicates the involving of the terminal oxygen from W=O_t bonds in the coordination to the vanadium ions. The $\nu_{as}(W{=}O_t)$ vibration band is broader in the complex spectra than the corresponding band in the ligand spectra because of its superposition with the stretching vibration $\nu_{as}(V{=}O)$ [7].

The tricentric W–O_c–W bonds of the corner-sharing WO_6 octahedra have different stretching vibrations in the two complexes. The $\nu_{as}(W{-}O_c{-}W)$ vibration is blue shifted with 19 cm^{-1} in the complex **1** FTIR spectrum compared to the ligand spectrum, and with 40 cm^{-1} in the complex **2** FTIR spectrum. This behavior arrises from different deformations induced by the vanadium ions coordination in the frame of the monolacunary ligands. The increase of the $\nu_{as}(W{-}O_c{-}W)$ frequency in the complexes indicates the shortening of these bonds after the metallic ion complexation [9]. Two vibration bands for the tricentric W–O_c–W bonds of the edge-sharing WO_6 octahedra are observed in the FT-IR spectrum of the **2** complex, while the complex **1** spectrum contains a single band. This suggests the presence in the **2** complex of two nonequivalent W–O_c–W bonds.

Two vibration bands for the tricentric W–O_e–W bonds of the edge-sharing WO_6 octahedra are observed in the FTIR spectra of the both complexes, like as in the ligand spectra. This suggests the presence in the complexes and in ligands of two nonequivalent W–O_e–W bonds [10]. Bindings from the cap region (with three octahedra) and the bondings from the belt region (with six octahedra) present a lower frequency of the trivacant Keggin and Dawson units than in the ligand, because of the coordination of each vanadium ion in the lacunary region of the ligands at oxygen atoms from corner-sharing octahedral [11]. The shifting of the W-O_e-W bands towards shorter energies in complexes compared by ligands shows a lengthening of the bonds.

The W–O_i bonds, where O_i connects the tungsten and silicon atoms, present two vibrations in the ligands and in complexes, too (Table 2), which confirms the coordination of vanadium ions in the lacunary region of the Keggin fragments.

The shifting of the bands in the complexes, compared by ligands suggests the implication of oxygen atoms O_t, O_c and O_e to VO^{2+} coordination. In complex **2** because Si-O_i band is shifted, it can be said that O_i atoms are implicated on VO^{2+} coordination.

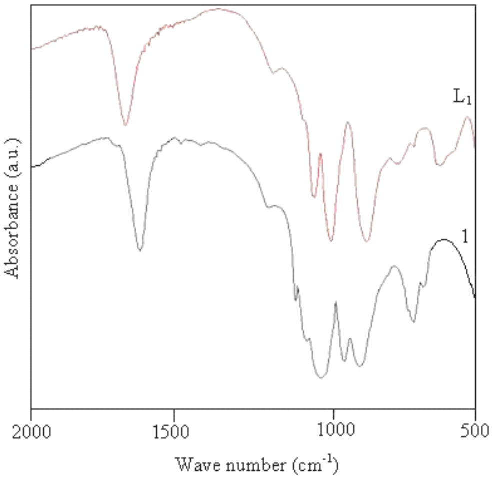

*Fig. 3. IR Spectra of the **L1** and **1** complex.*

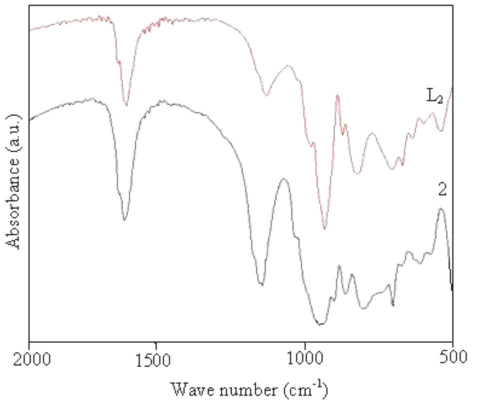

*Fig. 4. IR Spectra of the **L2** and **2** complex.*

Table 2. FT-IR bands (cm^{-1}) of the ligand and vanadium–HPOM complexes [a].

Band	L_1	1	L_2	2
$\nu_{as}(Si{-}O_i)$	1103w	1109w	1113s	1113m 951 m
$\nu_{as}(W{=}O_t)$	947s	968s	973sh	951m
$\nu_{as}(W{-}O_c{-}W)$	887vs,br	906v s	901 vs 841 m,	903 vs, sp 835 m,
$\nu_{as}(W{-}O_e{-}W)$	796vs, 729s	783vs 669m	798 m, 727 s	781 s, 666 m

[a] *w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad; sp, sharp*

3.3 Electronic spectroscopy

The UV-electronic spectra of the ligands and complexes (Fig. 5, Table 3) exhibit two characteristic bands at ~200 nm and ~250 nm, assigned to W-O_t (ν_1) and W-O_b-W (ν_2) transitions respectively (O_t is a terminal oxygen and O_b is a bridging oxygen) [12]. In both polyoxometalate complexes the ν_1 band are shifted to higher frequencies by comparing with ligands and the ν_2 bands are shifted to lower frequencies due to the coordination of the vanadyl cations.

Table 3. Electronic absorbtion bands (cm^{-1}) in UV spectra.

Band	L$_1$	1	L$_2$	2
ν_1 (M-O$_{c,e}$–M)	38680 sh 36800 sh	38480	34040sh	34000sh
ν_2 (M-O$_t$)	47680	47680	47040	47440

^{a} *w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad; sp, sharp*

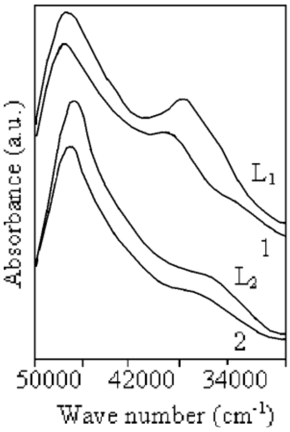

Fig. 5. UV spectra of the potassium salt of the (VO)SiMo$_2$W$_9$ (1), VOSi$_2$MoW$_{16}$ (2) and of the potassium salt of the SiMo$_2$W$_9$ (L$_1$), Si$_2$MoW$_{16}$ (L$_2$), obtained in 5x10^{-5} mol·l^{-1} aqueous solution.

The visible electronic spectra of both complexes (Figure 6) shows a relative stronger absorption above 16000 cm^{-1} and a band with a shoulder at lower wavenumbers. The strong absorptions correspond to the $V^{IV} \rightarrow W^{VI}$ charge transfer transitions [9]. The analyses of the spectra lead to obtaining the position of the bands for V^{IV} ions d-d transitions. 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 O$_h$ local symmetry [13]. 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.

Studying the visible spectrum of the $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ complex it can be said that this compound has an O$_h$ distorted symetry. The ν_1 band, from 13 500 cm^{-1} is shifted towards shorter energy compared by $[VO(H_2O)_5]^{2+}$ aquaion, and it is a very weak band, like a shoulder. It is atributed to $^2B_{1g} \leftarrow {}^2B_{2g}$ transition. The ν_2 band, from 15 400 cm^{-1} is shifted towards shorter energy compared by $[VO(H_2O)_5]^{2+}$ aquaion, and it is like a shoulder. That is due to the $^2A_{1g} \leftarrow {}^2B_{2g}$ transition. The ν_3 band, from 18 800 cm^{-1} is very strong on intensity, and it can be atributed to the $^2T_{2g} \leftarrow {}^2E_g$ transition.

In the visible spectrum of the $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$ complex there are three bands:

$$\nu_1 = {}^2B_{1g} \leftarrow {}^2B_{2g} = 13\ 800\ \text{cm}^{-1}$$
$$\nu_2 = {}^2A_{1g} \leftarrow {}^2B_{2g} = 15\ 800\ \text{cm}^{-1}$$
$$\nu_3 = {}^2T_{2g} \leftarrow {}^2E_g = 23\ 200\ \text{cm}^{-1}$$

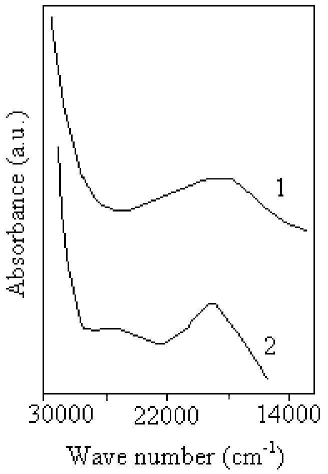

Fig. 6. Visible electronic spectra of the vanadium-HPOM complexes in 10^{-2} mol·l^{-1} aqueous solution.

3.4 EPR spectra

Some EPR parameters of the one-electron-reduced anion at room and liquid nitrogen temperatures have been reported by Cadot et all [2, 14]. They have obtained an axial spectrum typical for V^{IV} ion, with resolved hyperfine features.

The now-reported powder EPR spectrum of the **1** complex at room temperature reveals the presence of a new reduced species as the above electronic studies suggest. This spectrum (Figure.7) is a superposition of one axial component with resolved V^{IV} hyperfine structure and one isotropic and very broad component [15-16].

The axial spectrum exhibits eight hyperfine components both in the perpendicular and the parallel bands due to the hyperfine coupling of the unpaired electron with the nuclear spin (I = 7/2) of the ≈ 99.8 % natural abundant ^{51}V isotope.

The best fit of EPR spectrum was made considering the $g_{//}$ = 1.920, $g_{\perp}$ =1.974, $A_{//}$ = 180 G, $A_{\perp}$ = 64 G, parameters and $\Delta B_{//}\ (p\text{-}p)$ = 30 G, $\Delta B_{\perp}(p\text{-}p)$ = 33 G linewidths for the axial component, g_{iso} = 1.974, $\Delta B_{iso}(p\text{-}p)$ = 452 G for the isotropic signal and Gaussian type line shapes. The two components contribute in the same amount (50%) to the whole spectrum, suggesting that the one-electron and the monoprotonated two-electron reduced species appear in equal quantity in the sample. The principal axes of ***g*** and ***A*** tensors were presumed coincident for the simulation of the axial spectrum, with $g_{//}$ direction parallel to the V=O_d bond.

The spectrum of the **2** complex exhibits eight components, both in the perpendicular and in the parallel bands, due to the metallic hyperfine coupling of the electron spin with the nuclear spin (I=7/2) of the 99.75 % natural abundant ^{51}V izotope. The absence of Mo^{5+} and W^{5+} EPR signals confirms that all the molybdenum and tungsten atoms are in the +6 oxidation state. The best fitting simulated EPR parameters are: g_{II}=1.940, $g_{\perp}$=1.982, A_{II}=178.5 G, $A_{\perp}$=62.9 G, with the line widths $\Delta B_{pp}(II)$=52 G and $\Delta B_{pp}(\perp)$=38 G in the parallel and perpendicular bands respectively. The principal axis of **g** and **A** tensors have been presumed coincident, with the g_{II} and A_{II} directions parallel to the V=O_d bond. Diferences between the experimental and simulated spectra indicate a small rhombic distortion of the VO_6 octahedron.

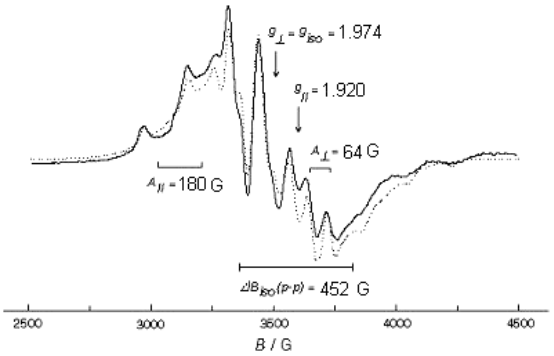

*Fig. 7. Experimental EPR spectrum of the powder VIV–HPOM **1** complex, at room temperature (normal line) and its simulated spectrum (dashed line).*

4. Conclusions

Were synthesised two new polyoxometalates with mixed addend atoms that have Keggin structure $K_6[Si(VO)Mo_2W_9O_{39}]\cdot 14H_2O$ and respectivelly Dawson structure $K_{10}[Si_2(VO)MoW_{16}O_{61}]\cdot 18H_2O$.

These complexes and their ligands have been investigated by means of elemental analysis and spectroscopic methods (FTIR, UV, VIS, EPR).

The analysis of the coordination mode of the vanadium ions was made by comparing the FT-IR spectra of the complexes **1** and **2** with those of the ligands. The shifting of the W-O_e-W bands towards shorter energies in complexes compared by ligands shows a lengthening of the bonds.

The UV-electronic spectra of the ligands and complexes exhibit two characteristic bands at ~200 nm and ~250 nm, assigned to W-O_t (ν_1) and W-O_b-W (ν_2) transitions, respectively. In both polyoxometalate complexes the ν_1 band are shifted to higher frequencies by comparing with ligands and the ν_2 band are shifted to lower frequencies due to the coordination of the vanadyl cations.

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The EPR spectra of both complexes are axial spectra and exhibits eight hyperfine components both in the perpendicular and the parallel bands, due to the hyperfine coupling of the unpaired electron.

Informations obtained from EPR lead to the establishment of intermolecular metal-metal interactions.

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