



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

SYNTHESIS AND CHARACTERIZATION OF THE POTASSIUM 11-TUNGSTOVANADO (IV) PHOSPHATE

Dan RUSU, ^aOana BĂBAN, ^bIoan HAUER, ^cDelia GLIGOR, ^dLeontin DAVID ^c and Mariana RUSU ^{*b}

^aIuliu Hatieganu University, Faculty of Pharmacy, 13 Emil Isaac Str., Cluj-Napoca 400023, Roumania

^bBabes-Bolyai University, Faculty of Chemistry and Chemical Engineering,
11 Arany Janos Str., Cluj-Napoca 400028, Roumania

^cBabes-Bolyai University, Faculty of Physics, 1 Mihail Kogalniceanu Str., Cluj-Napoca 400084, Roumania

^dBabes-Bolyai University, Faculty of Environmental Science, 30 Fântânele Str., Cluj-Napoca 400294, Roumania

Received March 30, 2010

The $K_5[PV^{IV}W_{11}O_{40}] \cdot 14H_2O$ polyoxotungstophosphate was synthesized, by the direct addition of vanadyl sulfate to a solution of the sodium salt of trilacunary α -Keggin polyoxotungstate anion, and analyzed by means of elemental analysis, IR, UV-VIS, EPR, ^{31}P -NMR spectroscopies and cyclic voltammetric measurements.

This allowed for determining subsequently the behavior of the encapsulated vanadium(IV) metal ions, their coordination by the Keggin fragments, the corresponding local symmetry, the type of metal-metal interactions and electrochemical redox behavior.

INTRODUCTION

Polyoxometalates are metal-oxygen clusters that exhibit a fascinating variety of structures and properties, including size, shape, charge, density, acidity, redox states, stability, solubility, etc. Transition metal substituted polyoxometalates (TMSPs) have attracted a continually growing interest in the field of polyoxometalate chemistry, being of great interest in catalysis, material science and medicine.¹⁻⁴

Baker⁵ has noted as early as 1973 that, in substituted Keggin anion $[(M^{n+}OH_2)PW_{11}O_{39}]^{(n-7)-}$, where M^{n+} as a hetero-metal is bonded in a pseudo-porphyrin environment. A substantial amount of work has been performed in the last 30 years to prepare and characterize substituted Keggin polyoxotungstate species.⁶

Over the past ten years, most of the attention was given to functionalize these compounds and to study their applications.⁷⁻¹²

Pope synthesized the first vanadium (IV) tungstophosphate³ by electrochemical method from $K_4[PV^VW_{11}O_{40}]$ as precursors, and Domaille obtained the same compound from $H_3[PW_{12}O_{40}]^{3-}$ and VO^{2+} cations in the presence of Li_2CO_3 .⁴

The aim of the present paper is to report a new preparation method for the potassium salt of the mono-substituted α -Keggin tungstophosphate $K_5[PV^{IV}W_{11}O_{40}] \cdot 14H_2O$ by the addition of the vanadyl ions to the trilacunary α -Keggin polyoxotungstophosphate.

RESULTS AND DISCUSSION

Vanadium(IV) cations react with α - $[P^VW_9O_{34}]^{9-}$ in aqueous solution according to the following equation:

* Corresponding authors: mrusu@chem.ubbcluj.ro or drusu@umfcluj.ro



The final product was isolated as potassium salt with a good yield. The elemental analysis of the complex is consistent with the proposed formula, $\text{K}_5[(\text{VO})\text{PW}_{11}\text{O}_{39}] \cdot 14\text{H}_2\text{O}$. Thermal study of the complex reveals the presence of 14 molecules of crystal (lattice) water molecules.

The following abbreviation will be used: i) for the anions: L_1 for $\alpha\text{-}[\text{P}^{\text{V}}\text{W}_9\text{O}_{34}]^{9-}$, L_2 for $\alpha\text{-}[\text{P}^{\text{V}}\text{W}_{11}\text{O}_{39}]^{7-}$, $\mathbf{1}$ for $[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$, ii) for the salts: Na_8HL_1 for $\text{Na}_8\text{H}[\text{PW}_9\text{O}_{34}] \cdot 14\text{H}_2\text{O}$, K_7L_2 for $\alpha\text{-K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 11\text{H}_2\text{O}$, $\text{K}_5\mathbf{1}$ for $\text{K}_5[(\text{VO})\text{PW}_{11}\text{O}_{39}] \cdot 14\text{H}_2\text{O}$.

The reaction mechanism must involve V (IV) metal cations insertion and transformation of the trilacunary $[\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ to the monolacunary $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ fragment.

FT-IR Spectra

Information about the vanadium ion coordination was obtained by comparing the IR frequencies of the K_7L_2 ligand with this of the vanadium complex with α -Keggin tungstophosphate ligand. The infrared bands can be attributed to an α -Keggin structure, in accordance with literature.^{16,17}

The FT-IR spectrum of the $\text{K}_5\mathbf{1}$ polyoxometallate is shown in Fig. 1 and the characteristic IR vibration bands of $\text{K}_5\mathbf{1}$, as compared to those of the K_7L_2 ligand, are displayed in Table 1.

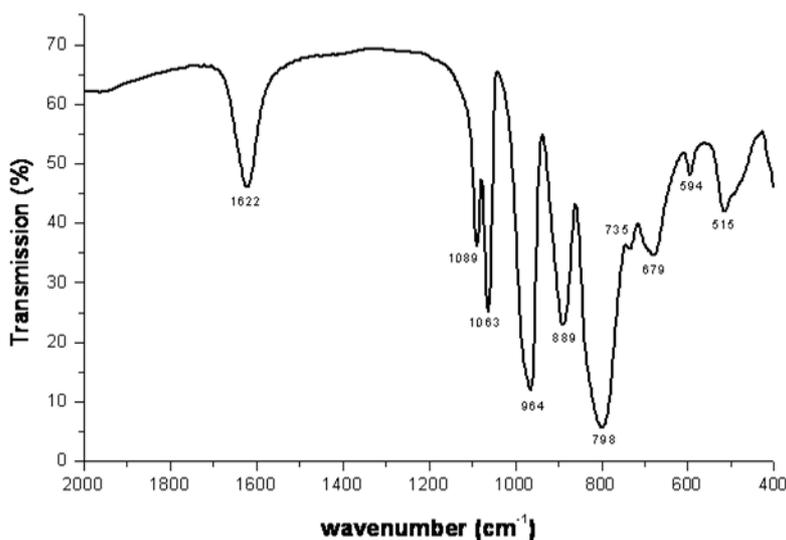


Fig. 1 – The FT-IR spectrum of the $\text{K}_5\mathbf{1}$ recorded in KBr pellets.

Table 1

Principal vibration bands observed in the FT-IR spectra (cm^{-1})

Vibration	K_7L_2^*	$\text{K}_5\mathbf{1}$
$\nu_{\text{as}}(\text{P-O}_i)$	1085 w, sp 1040 m, sp	1090 w, sp 1063 m, sp
$\nu_{\text{as}}(\text{W=O}_i)$	950 s	962 s, b
$\nu_{\text{as}}(\text{W-O}_c\text{-W})$	900 m 860 vs, b	889 m 798 vs, vb
$\nu_{\text{as}}(\text{W-O}_e\text{-W})$	810 w 725 w	735 w 679 w
$\delta(\text{O}_i\text{-P-O}_i)$	590vw	594 vw
$\delta(\text{W-O}_{c,e}\text{-W})$	510 w	515 w

Notes: w, weak; m, medium; s, strong; vs, very strong; b, broad; vb, very broad; sp, sharp; O_i is an internal oxygen which links P and W atoms, $\text{O}_{c,e}$ connects corner and edge-sharing octahedra, O_t is a terminal oxygen.

*18

The similarity of the FT-IR spectra for ligand K_7L_2 and for complex K_5I shows that the vibration bands are mainly due to the polyoxotungstate structure (Tab.1).¹⁸ All asymmetric frequencies bonds involving tungsten ions are shifted ($5-62\text{ cm}^{-1}$) in the complex spectrum compared to the ligand spectrum.

The shift of the $\nu_{as}(P-O_i)$ antisymmetric stretching vibrations, the main bands of the ligand, towards higher energies in the complex indicates that the coordination increases the cohesion of the monolacunary ligand structure.¹⁹ The tiny shift of the $\nu_{as}(W=O_t)$ stretching vibration in the spectrum of the complex, as compared to the ligand, can be explained by the fact that terminal O_t atoms are not involved in the coordination of vanadium ions. On the other hand, the larger shift of the $\nu_{as}(W-O_{c,e}-W)$ stretching vibrations, for the bonds from the belt and cap areas, indicates the coordination of vanadium metal ion by O_c and O_e oxygen atoms from corner-sharing and edge-sharing octahedra.²⁰

The shift of the frequencies for the tri-centric bonds in the FT-IR spectrum of the complex compared to the ligand spectrum is in accordance with the coordination of the vanadium ions in the lacunary regions of the monolacunary Keggin fragments.

Electronic Spectra

We have registered the electronic UV and VIS spectra on aqueous solutions of the potassium salt of the polyoxometalate K_5I and compared them with that of the ligand Na_7L_2 anion or with that of the $[VO(H_2O)_5]^{2+}$ aqua-cations.

The UV spectrum (insert in fig.2) exhibits the two charge transfer bands of the polyoxometalate anion.²¹ The UV bands of the K_5I complex, as compared to those of the K_7L_2 ligand, are listed in Table 2.

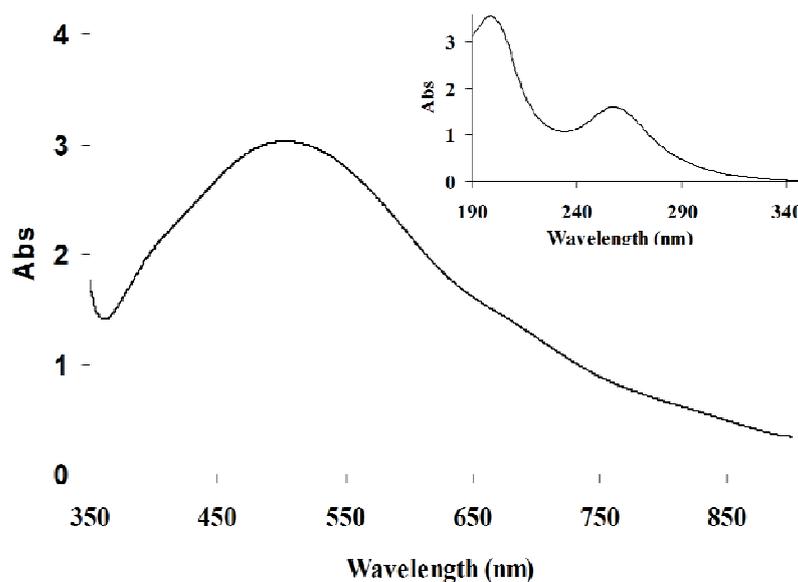


Fig. 2 – The UV-Vis spectra of the K_5I ($5 \cdot 10^{-5}$ - $5 \cdot 10^{-3}\text{ mol}\cdot\text{l}^{-1}$ aqueous solution).

Table 2

UV-Vis spectral features (cm^{-1}) of the K_5I and K_7L_2

Electronic transition	ν (cm^{-1})	
	$K_7L_2^*$	K_5I
$\nu_2: p_\pi \rightarrow d_\pi (M=O_t)$	50 251 / 199 (s)	50 377 / 198.5 (s)
$\nu_1: d_\pi \rightarrow p_\pi \rightarrow d_\pi (M-O_{c,e}-M)$	39 476 / 252 (m)	38 834 / 257.5 (m)
${}^2B_2(d_{xy}) \rightarrow {}^2A_1(d_z^2)$	-	24 752 / 404 (sh)
${}^2B_2(d_{xy}) \rightarrow {}^2A_1(d_x^2)$	-	19 880 / 503 (m)
${}^2B_2(d_{xy}) \rightarrow {}^2B_1(d_x^2 - y^2)$	-	15 527 / 644 (sh)
${}^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz}, d_{yz})$	-	13 440 / 744 (sh)

^a sh, shoulder; s, strong; m, medium.

* 21

The UV spectra of the ligand and complexes are also very similar, evincing that the charge transfer inside the polyoxotungstate structure is not significantly affected by coordination.

The higher energy band (ν_1) at $50\,377\text{ cm}^{-1}$, due to the $d\pi$ - $p\pi$ proper transitions from the $W=O_t$ bonds, insignificantly shifted in the complex, compared to the ligand, can be associated with the lack of involvement of the terminal oxygen atoms in the coordination of the cations of transitional metals.²²

The lower energy band (ν_2) at $38\,834\text{ cm}^{-1}$, due to the $d\pi$ - $p\pi$ - $d\pi$ electronic transitions from the tricentric $W-O_{c,e}-W$ bonds, with an expected absorption maximum in the range of $40\,000$ - $38\,000\text{ cm}^{-1}$, was shifted to lower frequencies in complex spectrum, compared to the ligand, and this is due to the decrease of the symmetry, as well as to the distortion of the WO_6 octahedra through complexation, which influences the electronic transfer from these bonds.

Visible spectra of the $K_5\mathbf{1}$ (Fig. 2) only show electron transfer bands of the V(IV) transition metal ions coordinated by the ligand.

The absorption bands of the $K_5\mathbf{1}$ complex as compared to those of the corresponding $[VO(H_2O)_5]^{2+}$ aqua-cations in octahedral field²³

and are listed in table 2. The two absorption bands at $13\,440$ and $15\,527\text{ cm}^{-1}$ are due to d-d transitions and correspond to the so-called bands I and II in normal oxovanadium complexes. The absorption bands at $19\,880$ and $24\,752\text{ cm}^{-1}$, which are responsible for the intense color of the anion, are assigned to the hetero-nuclear intervalence charge-transfer transitions $V(IV)\rightarrow W(VI)$.²² Due to that, the lowest energy for such a transition should be at about $20\,000\text{ cm}^{-1}$; the complex can be regarded as a "heteropoly blue".²⁴

EPR Spectroscopy

The powder EPR spectrum (Fig.3) of the complex recorded at X band and room temperature is typical for monomeric oxovanadium species in an axial environment. The spectrum exhibits eight components, both in the perpendicular and parallel bands, due to the metallic hyperfine coupling of the electron spin with the nuclear spin ($I_V=7/2$).

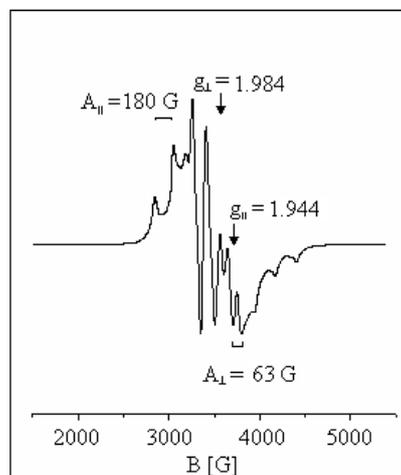


Fig. 3 – The EPR spectrum at room temperature of the $K_5\mathbf{1}$ complex.

This spectrum can be described by an axial Hamiltonian spin for a d^1 system²⁵:

$$\hat{H}_s = \beta[g_{||}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{||}S_zI_z = A_{\perp}(S_xI_x + S_yI_y)$$

where $g_{||}$, g_{\perp} and $A_{||}$, A_{\perp} are the axial principal values of the g and hyperfine tensors respectively, β 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 characteristic EPR parameters are $g_{\perp} = 1.984$, $g_{\parallel} = 1.944$, $A_{\perp} = 63$ G, $A_{\parallel} = 180$ G.

The electronic ground state for V^{4+} in a C_{4v} local symmetry is the anti-bonding B_2 molecular orbital formed by the d_{xy} orbital of the vanadium ion. The covalence degree of the in-plane V-O σ and π bonds and out-of-plane π bond with the vanadyl oxygen were evaluated by LCAO-MO model developed by Kivelson and Lee.²⁶ Considering the spin coupling constant $\lambda = 170$ cm^{-1} ,²⁷ $P = 0.128$ the dipolar interaction term, $K = 0.787$ the isotropic Fermi contact term, we obtained $\beta_1^2 = 0.865$, $\beta_2^2 = 0.877$ and $\beta_3^2 = 0.934$ for the in-plane σ -bonding, in-plane π -bonding and out-of-plane π -bonding respectively.

The out-of-plane π -bonding has a dominant ionic character, with the unpaired electron spending more time into the $d_{xy, yz}$ orbital of the vanadium ion.²⁸ These values show that the electron delocalization is towards the oxygen atoms from V-O_{b,c} bonds.²⁹

³¹P-NMR spectrum

The recorded ³¹P-NMR spectrum in D₂O show a major peak at -5.06 ppm. The peak at -5.06 ppm is attributed to K₅I if the complex remains intact in solution.

The ³¹P-NMR spectrum of the K₅I (Fig. 4) consist of single lines as expected with the considerably broadened as a result of V(IV) paramagnetism.

The ³¹P signal broadenings are explained in terms of the electronic spectroscopic state of the substituted vanadium (IV) cations. For the various complexes substituted Keggin polyoxometalate of given paramagnetic ion, increased line broadening accompanies increased change of chemical shift, relative to that for the corresponding diamagnetic cations, for the P atoms near the substitution sites. This effect is due to partial delocalization of unpaired electron spins.³⁰

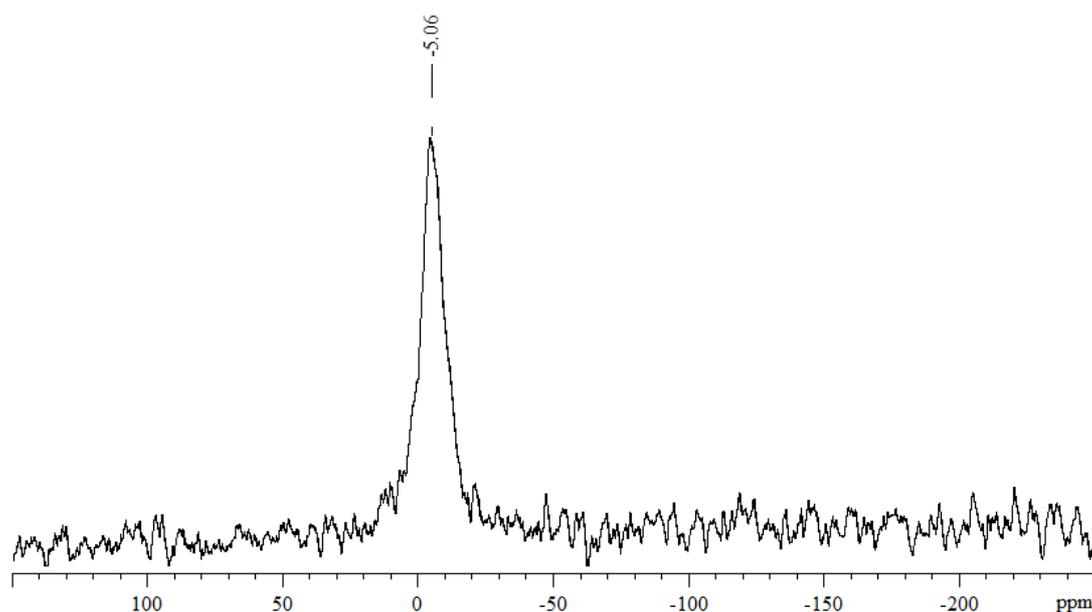


Fig. 4 – The ³¹P-NMR spectrum of the K₅I in D₂O.

Electrochemical behavior

Figures 5A and 5B present comparatively the cyclic voltammograms obtained for K₅I, in different potential ranges. As it can be observed from figure 5A, at high scan rates (for example, 400 mV s^{-1}), the cyclic voltammograms present four well-defined peak pairs, with the formal standard potential, E° , $[E^{\circ} = (E_{pc} + E_{pa})/2]$,³¹

where E_{pc} stands for the cathodic and E_{pa} for the anodic peak potential, placed in the negative domain, for peak pairs I-III and in positive domain, for peak pair IV.

Peak pairs I-III were attributed to the W^{+6}/W^{+5} processes^{32,33} and peak pair IV to $V^{+5} - V^{+4}$ ^{27,32} in the polyoxometalate framework.

The large positive shift of the E° values for peak pair IV suggest that vanadium is more

difficult to oxidize than tungsten. This behavior could be explained by some multi-electronic processes involved in V oxidation.³²

Where the potential range is selected between -400 mV and +1000 mV vs. SCE, it can be

observed (see figure 5B) that another peak pair appears, V, at ~ 600 mV vs. SCE (only at small scan rates). This can be attributed to $V^{+4} - V^{+3}$ reduction.

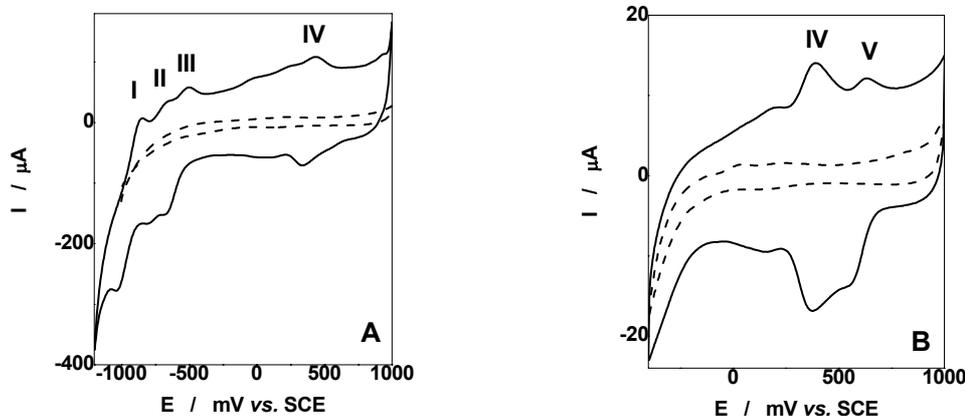


Fig. 5 – Cyclic voltammograms for 10^{-3} M K_5I solution (—) and for supporting electrolyte (---), on graphite electrode. Experimental conditions: starting potential, -1200 mV vs. SCE (A) and -400 mV vs. SCE (B); potential scan rate, 400 mV s^{-1} (A) and 50 mV s^{-1} (B); supporting electrolyte, acetate buffer solution (pH 4.5).

The values of ΔE_{peak} (see Table 3) show that the peak pair IV of K_5I presents a reversible electrochemical behavior ($\Delta E_p = 21 \text{ mV}$, at 50 mV s^{-1}), while the peak pairs I-III present a quasi-reversible electrochemical behavior. However, the reversibility degree is better for peak pair II (smaller ΔE_p value) in comparison with peak pairs I and III, reflecting a faster electron transfer in the first case.

In order to investigate the scan rate influence on the electrochemical behavior of K_5I , cyclic voltammetric measurements were performed in a

wide range of potential scan rates ($0.16 - 0.8 \text{ V s}^{-1}$ for peak pairs I-III and $0.16 - 2.56 \text{ V s}^{-1}$ for peak pair IV). The slopes of the $\log I_p$ vs. $\log v$ dependences for the polyoxometalate were close to the theoretical value (0.5) for all peak pairs, indicating diffusion-controlled processes (Table 3), except for peak pair II, where the redox process involved is a mixed one, being both diffusion- and surface-controlled.

Table 3

Log-log linear regression parameters for the dependence of the peak current on the potential scan rate ($0.16 - 0.8 \text{ V s}^{-1}$ for peak pairs I-III and $0.16 - 2.56 \text{ V s}^{-1}$ for peak pair IV) observed for K_5I . Experimental conditions: as in figure 5

Peak pair	Slope		R / no. of exp. points	
	oxidation	reduction	oxidation	reduction
I	0.41 ± 0.02	0.38 ± 0.03	0.996 / 5	0.996 / 3
II	0.79 ± 0.02	0.61 ± 0.09	0.999 / 4	0.975 / 4
III	0.56 ± 0.01	0.42 ± 0.06	0.997 / 5	0.988 / 3
IV	0.61 ± 0.04	0.43 ± 0.02	0.987 / 7	0.998 / 9

The electrochemical signal of vanadium is very distinct and creates favourable views for using it as a redox mediator for electrochemical polyoxometalate-modified electrodes.²⁷

For this, the influence of potential cycling on the electrochemical response of peak pairs IV and V corresponding to K_5I was investigated under

potential-dynamic conditions, by continuous cycling of the electrode potential, (25 cycles) in the potential range of -400 mV ÷ 1000 mV vs. SCE. A small decrease of the peak current was observed (Table 4), suggesting a good stability of polyoxometalate in acetate buffer solution (pH 4.5).

Table 4

Linear regression parameters for the dependence of peak current on cycling time, corresponding to compounds K_5I in solution, on graphite electrode. Experimental conditions: scan rate, 50 mV s^{-1} ; for the other conditions, see figure 5B

Peak pair	$I_{t=0}$ (10^6 A)		Slope (10^{10} A s^{-1})		R / no. of exp. points	
	oxidation	reduction	oxidation	reduction	oxidation	reduction
IV	4.6 ± 0.008	4.5 ± 0.02	1.7	3.2	0.989 / 10	0.994 / 5
V	1.5 ± 0.0005	2.8 ± 0.02	4.1	5.2	0.962 / 7	0.991 / 6

EXPERIMENTAL

Methods

Elemental analysis of P, W, V, was performed by OES-ICP with a BIRD 2070 spectrophotometer, and K was determined by PerKin-Elmer Flame photometer 373 by FAES method ($\lambda = 766.5 \text{ nm}$). Water content was determined from weight loss by heated of the compound at 120°C .

FT-IR spectra were recorded on a Jasco FT/IR 615 spectrophotometer, in the $4000\text{--}400 \text{ cm}^{-1}$ range, using KBr pellets.

UV-VIS spectra were recorded in the $\lambda=190\text{--}900 \text{ nm}$ range, in aqueous solution ($5 \cdot 10^{-5} \text{ M}$ – $5 \cdot 10^{-3} \text{ M}$), using a standard UV-Vis JASCO V-670 spectrophotometer.

EPR spectra on powdered solids were recorded at room temperature in the X-band using a JOEL-JES-3B spectrometer (9.40 GHz). All g values have been estimated with a ± 0.002 precision.

^{31}P NMR spectrum in D_2O was recorded on Bruker AVANCE 300 spectrometer. Chemical shifts are reported in parts per million (ppm) and are referenced to H_3PO_4 (^{31}P) as external standards.

The cyclic voltammetry measurements were performed in a classical three-electrode electrochemical cell equipped with the working electrode (graphite), the reference electrode (a saturated calomel electrode, SCE) and Pt as counter electrode ($\sim 1 \text{ cm}^2$). The electrochemical cell was connected to a computer-controlled potentiostat (Autolab-PGSTAT10, Eco Chemie, Netherlands). The sample was a 1mM solution of the investigated polyoxometalate dissolved in acetate buffer (pH 4.5). The pH was measured using a combined glass electrode (Metrohm, Switzerland) and a digital pH-meter (MV-Präcitronic, Germany). All measurements were performed at room temperature and atmospheric pressure.

Materials

Reagents grade chemicals were used and all synthesis and studies were carried out in distilled water.

Synthesis of the $K_5[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$

The synthesis of the title compound was performed in an aqueous solution at a pH level of 4.5. The lacunary Na_8HL_1 was obtained following, $^{15} \text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Merk) and KCl were used as received.

$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (0.76 g, 3 mmol) was dissolved in water (10 ml) and added dropwise, while stirring, to an aqueous solution (20 ml) of $\text{Na}_8\text{H}[\text{PW}_9\text{O}_{34}]$ (5.34 g, 2 mmol). The pH was adjusted to 4.5 with a 0.5 M HCl solution. The mixture was heated at 50°C for 20 minute and then was cooled to room temperature. Then solid potassium chloride 3 g (40 mmols)

was added while stirring. After standing for 2 hours at room temperature, a brown powder was obtained by filtration and washed with KCl 2M.

From filtrate solutions, after five days at room temperature, purple–red parallelepipedic crystals of $K_5[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$ were collected.

Chemical analysis:

K_5I found (calculated): K 6.12 (6.12), P 1.02 (0.97), V 1.48 (1.59), W 63.46 (63.35), H_2O 7.88 (7.90).

CONCLUSIONS

This work reports the synthesis and characterization of the potassium salt of the vanadium monosubstituted α -Keggin tungstophosphate $K_5[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$, a very interesting compound, because of the catalytic and biologic properties of the vanadium element.

The V(IV) substituted Keggin polyoxotungstophosphate in aqueous solution: was synthesized, by the direct addition of vanadyl sulfate to a solution of the trilacunary α -Keggin polyoxotungstate anion, and analyzed by means of elemental and thermogravimetric analysis, IR, UV-VIS, EPR and ^{31}P -NMR spectroscopies and cyclic voltammetric measurements.

Elemental analysis is in good agreement with calculated values for proposed molecular formula of $K_5[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$.

The IR spectra show that the α - $K_7[\text{PW}_{11}\text{O}_{39}]$ act as pentadentate ligand involving the oxygen atoms of monolacunary cavity.

Electronic and EPR spectra indicate O_h local symmetry for vanadium ion in $K_5[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$ compound.

The EPR and ^{31}P -NMR spectra confirm that the unpaired electron delocalization is towards the oxygen atoms from V– $\text{O}_{b,c}$ bonds.

The redox behavior of the newly synthesized polyoxometalate recommends it as a promising mediator (electrocatalyst) in indirect electrochemical reactions.

REFERENCES

1. M.T. Pope, "Heteropoly and Isopoly Oxometalates", Springer-Verlag, Berlin, 1983.
2. M. T. Pope and A. Müller, *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 34.
3. C. Hill, "Polyoxometalates", Ed: Chemical Reviews; American Chemical Society, Washington, D.C. 1998.
4. M. T. Pope and A. Müller, "Polyoxometalates: from Platonic Solids to Anti-Retroviral Activity", Eds. Kluwer, Dordrecht, Netherlands, 1994.
5. L.C.W. Baker, *Proc. XV Int. Conf. Coord. Chem.*, **1973**.
6. L.C.W. Baker and D. Glick, *Chem. Rev.*, **1998**, *98*, 3 (and references therein).
7. J.A.F. Gamelas, M.S. Balula, M. Carapuça and A.M.V. Cavaleiro, *Electrochem. Comm.*, **2003**, 5378.
8. V. Artero, D. Laurencin, R. Villanneau, R. Thouvenot, P. Herson, P. Gouzerh and A. Proust, *Inorg. Chem.*, **2005**, *44*, 2826.
9. G. Sazani and M.T. Pope, *J. Chem. Soc.*, *Dalton. Trans.*, **2004**, 1989.
10. C. Zang, R.C. Howell, K.B. Scotland, F.G. Perez, L. Todaro and L.C. Francesconi, *Inorg. Chem.*, **2004**, *43*, 7691.
11. C.L. Hill, *Angew. Chem. Int. Ed.*, **2004**, *43*, 402.
12. D. Jabbour, B. Keita, I.-M. Mbomekalle, L. Najdo and U. Kortz, *Eur. J. Inorg. Chem.*, **2004**, 20036.
13. D. P. Smith and M.T. Pope, *Inorg. Chem.*, **1973**, *12*, 331.
14. P.J. Domaille, *J. Am. Chem. Soc.*, **1984**, *106*, 7677.
15. R.G. Finke, M.W. Droegge and P.J. Domaille, *Inorg. Chem.*, **1987**, *26*, 3886.
16. C. Rocchiccioli-Deltcheff, M. Fournier and R. Franck, *Inorg. Chem.*, **1983**, *22*, 207.
17. R. Thouvent, M. Fournier, R. Franck and C. Rocchiccioli-Deltcheff, *Inorg. Chem.*, **1984**, *23*, 598.
18. C. Rocchiccioli-Deltcheff and R. Thouvenot, *J. Chem. Res. (S)*, **1977**, 47.
19. C. Rocchiccioli-Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta.*, **1976**, *32A*, 587.
20. W.H. Knoth, P.J. Domaille and R.L. Harlow, *Inorg. Chem.*, **1986**, *25*, 1577.
21. M. Rusu, "Heteropolytungstates with U(IV) as central atoms", Ph.Thesis, Babes-Bolyai Univ. Cluj, Roumania, 1975.
22. H. So and M.T. Pope, *Inorg. Chem.*, **1972**, *11*, 1441.
23. B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, 1984.
24. G.M. Varga, Jr., E. Papaconstantinou and M.T. Pope, *Inorg. Chem.*, **1970**, *9*, 662.
25. A. Bencini and D. Gatteschi, "Transition Metal Chemistry", vol. 8, Marcel Dekker, New York, 1982.
26. D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **1964**, *41*, 1896.
27. L. David, C. Craciun, M. Rusu, O. Cozar, P. Ilea and D. Rusu, *Polyhedron*, **2000**, *19*, 1917.
28. J. Park and H. So, *Bull. Koorean Chem. Soc.*, **1994**, *15*, 5643.
29. C. Rong and M.T. Pope, *J. Am. Chem. Soc.*, **1992**, *114*, 2932.
30. T.J. Jorris, M. Kozik, N. Casan-Pastor, P.J. Domaille, R.G. Finke, W.K. Miller and L.C.W. Baker, *J. Am. Chem. Soc.*, **1987**, *109*, 7402.
31. R. W. Murray, "Electroanalytical Chemistry", Ed. Marcel Dekker: New York, 1984, 191.
32. O. Serdan, D. Rusu, P. Ilea and I.C. Popescu, *Annals West Univ. Timisoara*, **2003**, *12*, 701.
33. A.R. Tomsa, A. Koutsodimou, P. Falaras, M.-C. Bernard and M. Rusu, *Synth. React. Inorg., Metal-Org. Nano-Metal Chem.*, **2005**, *35*, 65.