

Synthesis and characterization of new vanadium salicyldoxime based complexes isolated by hydrothermal process.

Synthèse et caractérisation de nouveaux complexes à base de vanadium et de la salicyldoxime isolés par voie hydrothermale.

Sultana Boutamine, Hennia Slaouti*, Ilyes Belkhattab & Zakia Hank

Université des Sciences et de la Technologie Houari Boumédiène, USTHB, Laboratoire d'Electrochimie, Corrosion, Métallurgie et Chimie Minérale, Faculté de Chimie, BP 32, El Alia, Bab Ezzouar 16111, Alger, Algeria.

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المخلص

في هذا العمل ، قمنا بدراسة تفاعل ساليسيلالدوكسيم على الباناديوم (V). عدة معقدات تم التحصل عليها اثر هذا التفاعل و تم تشخيصها باستخدام التحليل الدقيق اشعة تحت الحمراء و فوق البنفسجية ، و للعناصر (كربون ، هيدروجين ، ازوت) ، و كذا وقد تم اقتراح الصيغ للمعقدات

الكلمات المفتاحية : ساليسيلالدوكسيم ، الباناديوم ، معقدات الباناديوم

Résumé

Dans ce présent travail, nous avons étudié la réactivité de la salicyldoxime ($C_7H_7NO_2$)(H_2L^1) sur des solutions aqueuses de vanadium(V) par voie hydrothermale. Deux adduits de formules respectives, $Na_4[V_6^{IV}V_4^VO_{22}H_2(OH)_6(C_7H_6O_2)_2(C_7H_5NO)] \cdot 6H_2O$ noté (A1) et $H_6[V_3^{IV}V_7^VO_{25}(OH)_3(C_7H_8NO_2)(C_7H_5NO)_2(C_7H_6O_2)] \cdot 5H_2O$ noté (A2) ainsi qu'un complexe de nature trimérique $[V_3O_5(C_7H_5NO)_3(C_7H_4NO_2)_3(C_7H_7NO_2)_3] \cdot (H_2O)$ noté (C1), ont été obtenus. Ces composés ont été caractérisés par différentes méthodes : Analyse élémentaire, conductivité molaire, spectroscopie IR, RMN du proton, du carbone et du métal, spectroscopie UV-visible, RPE, spectroscopie de masse et par voltammetry cyclique

Key words: salicyldoxime, complexes de vanadium et synthèse hydrothermale.

Abstract

In this paper, the results of a systematic study of the reactivity of salicyldoxime ($C_7H_7NO_2$)(H_2L^1), with aqueous solutions of V(IV) using hydrothermal synthesis are reported.

These reactions lead to the formation of gray-blue compounds : (1) adduct of the formula $Na_4[V_6^{IV}V_4^VO_{22}H_2(OH)_6(C_7H_6O_2)_2(C_7H_5NO)] \cdot 6H_2O$ (A1), (2) another adduct of formula $H_6[V_3^{IV}V_7^VO_{25}(OH)_3(C_7H_8NO_2)(C_7H_5NO)_2(C_7H_6O_2)] \cdot 5H_2O$ (A2) and (3) a trimetric coordination complex of the formula $[V_3O_5(C_7H_5NO)_3(C_7H_4NO_2)_3(C_7H_7NO_2)_3] \cdot (H_2O)$ (C1).

The obtained compounds were characterized by means of elemental analysis, conductometry, UV-Visible, Fourier transform infrared absorption spectroscopy (FTIR), 1H and ^{51}V nuclear magnetic resonance (NMR), EPR, magnetic measurements, mass spectroscopy and cyclic voltammetry.

Key words: hydrothermal synthesis, vanadium complexes, salicyldoxime.

* Corresponding author : henniam@yahoo.fr

1. INTRODUCTION

Vanadium compounds are extensively studied because of their interesting redox, electrochemical, and catalytic or magnetic properties.

An ever-increasing research interest in the coordination chemistry of vanadium has been aroused not only due to its exhibiting a range of oxidation states from +5 to -1 but also from the fascinating structural novelties and complexities exhibited by vanadium complexes and their immense biological, [1,2] industrial, [3,4] and medicinal applications [5,6]. For vanadium, +4 oxidation state is the most stable while lower oxidation states are strongly reducing and are stable only at low temperatures. The coordination chemistry and reactivity of low-valent vanadium, +3, are known to display interesting reactivity behavior, such as the capability of dinitrogen fixation, [7–9] in particular, with anionic oxygen donors [10].

The increasing interest in hydrothermal synthesis derives from its advantages in terms of high reactivity of reactants, easy control of solution or interface reactions, formation of meta-stable and unique condensed phases, less air pollution, and low energy consumption. In addition to lowering the overall cost of the synthesis process, the low reaction temperatures avoid common problems encountered with high-temperature technologies, such as poor stoichiometric control due to volatilization of components, presence of thermally induced defects, formation of undesired phases, and unwanted phase transformations.

There are many studies that have been done on hydrothermal synthesis of materials with the particular magnetic and electronic properties are reported in the literature [11,12].

Vanadium oxide chemistry is characterized by several general families of compounds: binary oxides, bronzes, and molecular polyanions. The chemistry of polyanions is vast and has been reviewed [13]. Representative examples of vanadate cluster chemistry include divanadate, $(V_2O_7)^{4-}$ [14], tetravanadate $(V_4O_{12})^{4-}$ [4] and decavanadate $(V_{10}O_{28})^{6-}$ [9].

The hydrothermal reaction of a mixture of vanadyl sulfate ($VOSO_4$) and vanadium chloride (VCl_3) with salicylaldehyde ($C_7H_7NO_2$) leads to the formation of various oxovanadium compounds, frequently hexacoordinated. About a trinuclear complex containing the core $V_3^{IV}O^{3+}$, and two compounds of high nuclearity based on the decavanadate ion are identified especially, by the elemental analysis, and by nuclear magnetic resonance (NMR) of ^{51}V . These decanuclear systems are the result of the high reactivity of salicylaldehyde at 100°C during 48 to 72 hours. The properties of solid state materials mainly depend on their structure and morphology. Before approaching the structural study of these particular compounds and to better understand their originality, we remind, briefly, the results published by Maity and al [1], who relate for two clusters of decavanadate.

Our attempts of characterization by ^{13}C NMR of the compounds treated in this study failed, because of their limited solubility in water and most organic solvents.

2. EXPERIMENTAL

2.1. reagents and general procedures

The reagents and solvents used were pure Fluka products. The initial concentrations of aqueous solutions of vanadium and those of salicylaldehyde in ethanol, were 2M. All reactions were performed at room temperature by adding the aqueous vanadium solution to ethanol solution containing the ligand. The pH of the aqueous solution was previously adjusted. The ligand/metal ratio was equal to 1:1. The reactional mixtures were heated under hydrothermal conditions. After cooling, the resulting mixture was opened, and solid products were filtered, washed several times with distilled water, and finally dried at 80°C.

2.2. analytical and physical measurements

The elemental microanalysis and mass spectra (electrospray method) were carried out at the central service of CNRS (France). Melting points were measured using an electro-thermal Buchi 512 apparatus.

The conductometry measurements were carried out with a CD 810 Tacussel conductometer. The 1H NMR solution spectra in $CDCl_3$ were recorded at 295 K on a Bruker AM 300 spectrometer with TMS

as reference. The ^{51}V NMR spectra were measured in D_2O or in DMSO-d_6 , using VOCl as the reference. The electronic absorption spectra in DMSO solution were recorded on a Perkin Elmer Lambda 9 spectrometer using supasil cells. The EPR spectra were recorded with a Bruker ER 200 spectrometer. Cyclic voltammetry was performed with Tacussel equipment consisting of a Tacussel PRT 24-1 potentiostat and GSATP generator. The infrared absorption spectra of KBr pellets were studied in the range of $4000\text{-}400\text{cm}^{-1}$ using a FTIR spectrometer (Perkin Elmer).

3. SYNTHESIS

3.1. Synthesis of (A1): $\text{Na}_4[\text{V}_6^{\text{IV}}\text{V}_4^{\text{V}}\text{O}_{22}\text{H}_2(\text{OH})_6(\text{C}_7\text{H}_6\text{O}_2)_2(\text{C}_7\text{H}_5\text{NO})].6\text{H}_2\text{O}$ compound

In the polyethylene hermetic reactors, 5cm^3 of a bleu solution of VOSO_4 (10^{-2} mol, 1.573 g) were introduced to 5cm^3 of an ethanolic solution of salicylaldoxime $\text{C}_7\text{H}_7\text{NO}_2$ (10^{-2} mol, 1.37g). The pH was adjusted at 3 using NaOH (2M), the resulting solution was then stirred at ambient temperature for 3 hours. The reaction mixture was kept at 100°C for 72 hours. This mixture was loaded into a 125cm^3 Teflon-lined autoclave.

3.2. Synthesis of (A2): $\text{H}_6[\text{V}_3^{\text{IV}}\text{V}_7^{\text{V}}\text{O}_{25}(\text{OH})_3(\text{C}_7\text{H}_8\text{NO}_2)(\text{C}_7\text{H}_5\text{NO})_2(\text{C}_7\text{H}_6\text{O}_2)].5\text{H}_2\text{O}$ compound

A similar procedure was adopted for the synthesis of A2. In the polyethylene hermetic reactors, 5cm^3 of a bleu solution of VCl_3 (10^{-2} mol, 1.63 g) were introduced to 5cm^3 of an ethanolic solution of salicylaldoxime $\text{C}_7\text{H}_7\text{NO}_2$ (10^{-2} mol, 1.37g). The pH was adjusted at 3 using NaOH (2M). The Reaction mixture was kept at 100°C for 48hours. This mixture was loaded into a 125cm^3 Teflon-lined autoclave.

3.3. Synthesis of C1: $[\text{V}_3\text{O}_5(\text{C}_7\text{H}_5\text{NO})_3(\text{C}_7\text{H}_4\text{NO})_3(\text{C}_7\text{H}_7\text{NO}_2)_3].\text{H}_2\text{O}$ compound

In the polyethylene hermetic reactors, 5cm^3 of a bleu solution of VOSO_4 (10^{-2} mol, 1.63 g) were introduced to 5cm^3 of an ethanolic solution of salicylaldoxime $\text{C}_7\text{H}_7\text{NO}_2$ (10^{-2} mol, 1.37g). The pH was adjusted at 2.5 by add of NaOH (2M). The reaction mixture was kept at 150°C for 24hours. The hydrothermal synthesis was achieved by heating each mixture under autogenous pressure in a static 125cm^3 Teflon-lined stainless steel autoclave.

Finally, the resulting powder materials were filtered off, washed several times with distilled water until neutral pH and dried at 80°C . The details of the synthesis and experimental results are shown in Table I.

Table I: Experimental condition for the Preparations of compounds.

Different compounds	Adduct A1	Adduct A2	Complex C1
Reaction time (hour)	72	48	24
Temperature ($^\circ\text{C}$)	100	100	150
pH before heating	3	3	2.5
pH after heating	6	4	6
Color of powder	Yellow-glass	Yellow-orange	Gray-blue

Table II gives the results of the elemental analyses and the physico-chemical properties of the different compounds. The limited solubility for the most part of these compounds in the usual solvents is due to their polynuclear structure that confirms the very high values of the melting points.

Table II: Elemental analyses and physico-chemical properties of the synthesized compounds.

Compounds	Empirical Formula	F.Wt	Colour	M.p (°C)	Molar conductance (ohm cm ⁻¹ mol ⁻¹)	Analytical data : calculated (found %)			
						C	H	N	V
A1	C ₂₁ H ₃₇ N ₁ O ₃₉ Na ₄ V ₁₀	1846	Yellow-glass	>400	255	16.48 (16.50)	02.42 (02.45)	00.92 (00.95)	33.36 (33.39)
A2	C ₂₈ H ₄₄ N ₃ O ₃₅ V ₁₀	1556	greenish-orange	>400	450	22.03 (22.05)	02.43 (02.45)	02.75 (02.78)	33.44 (33.45)
C1	C ₆₃ H ₅₃ N ₉ O ₁₈ V ₃	1375	Gray-blue	162	-	54.94 (55.00)	03.85 (03.88)	09.16 (09.18)	11.12 (11.13)

4. RESULTS AND DISCUSSION

4.1 Characterization of decanuclear compounds A1 and A2

Our decanuclear compounds, of adduct types will be studied with regard to the spectral data of salicylaldehyde (H₂L¹).

The exam of the IR spectra of Na₄[V₆^{IV}V₄^VO₂₂H₂(OH)₆(C₇H₆O₂)₂(C₇H₅NO)].6H₂O (A1) and H₆[V₃^{IV}V₇^VO₂₅(OH)₃(C₇H₈NO₂)(C₇H₅NO)₂(C₇H₆O₂)].5H₂O (A2) were recorded between 4000 and 1000 cm⁻¹. The vibrations recorded in A1 and A2 correspond to some fields changes with those of the spectra of adduct. Indeed, apart from the additional peak at 1570 cm⁻¹ in adduct A2, due to the C = N bond of the oxime, the spectrum of both adduct A1 (Fig.1) and adduct A2 (Fig.2) have the same profile characteristic of a hydrolysis reaction, singled by a ketone vibration around 1640 cm⁻¹ and dehydration identifiable by the presence of a nitrile group frequency at 2229 cm⁻¹. The extension vibrations corresponding to V=OR connections are duplicated in 1000 and 950 cm⁻¹ for A1, and at 990 and 953 cm⁻¹ for A2.

Correlated with the degree of oxidation of vanadium, and therefore its polarization effect, the vibrations around 1000 and 950 cm⁻¹ are attributed to the V^V = Ot bonds and V^{IV} = Ot, respectively.

From the IR data, the presence of the unaltered salicylaldehyde in A2 structure may seem logic priori seen as the synthesis' time did not exceed 48 hours. This time seems to be insufficient for a total transformation of the oxime. Moreover, the simultaneous presence, in these compounds, of metal-based polyanionic V₁₀O₂₈ system and organic ligands can be explained on the basis of the establishment of strong hydrogen bonding between the basic oxygen V₁₀O₂₈^{-x} and acidic protons of salicylaldehyde and its derived forms.

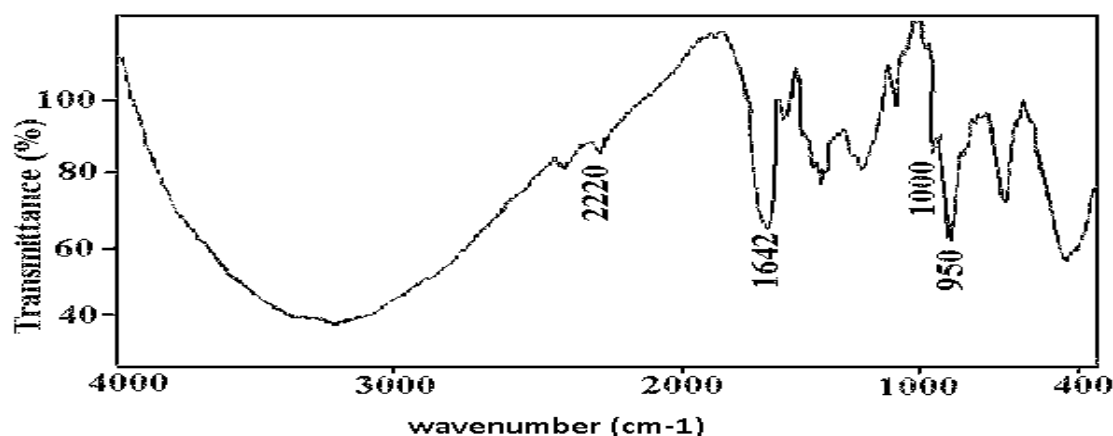


Figure.1: FTIR spectra of A1 in KBr pellet.

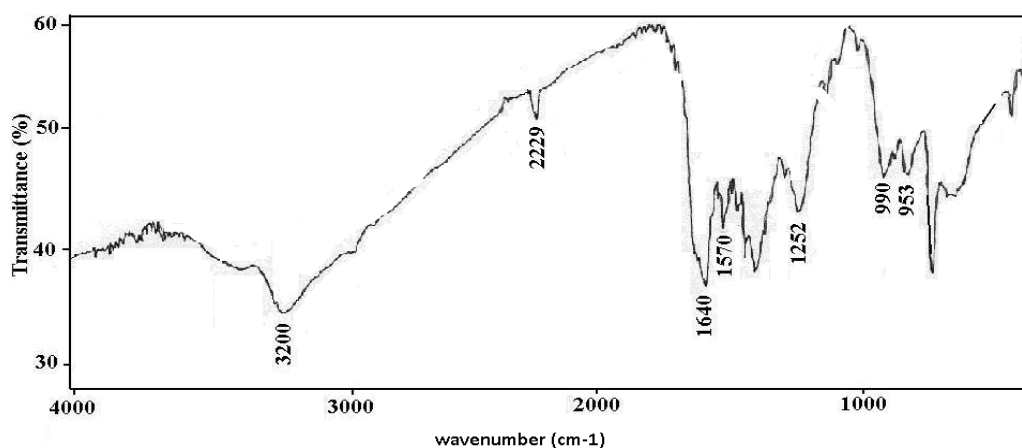
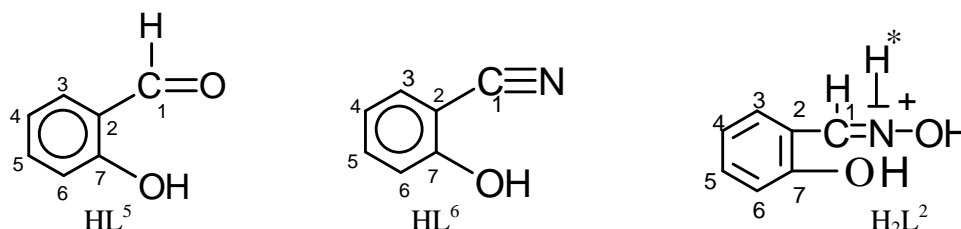


Figure.2: FTIR spectra of A2 in KBr pellet.

The ^1H NMR spectra of A1 and A2 in DMSO, are given in Figures 3 and 4, respectively. Note that the proton signals in the 6.5-8 ppm area, consisting of three massive and two massive with several lines from the non-equivalence of the hydrogen are well resolved. The other peaks, at lower field are singlets. The chemical shifts, consistent with structures given below are summarized in table III

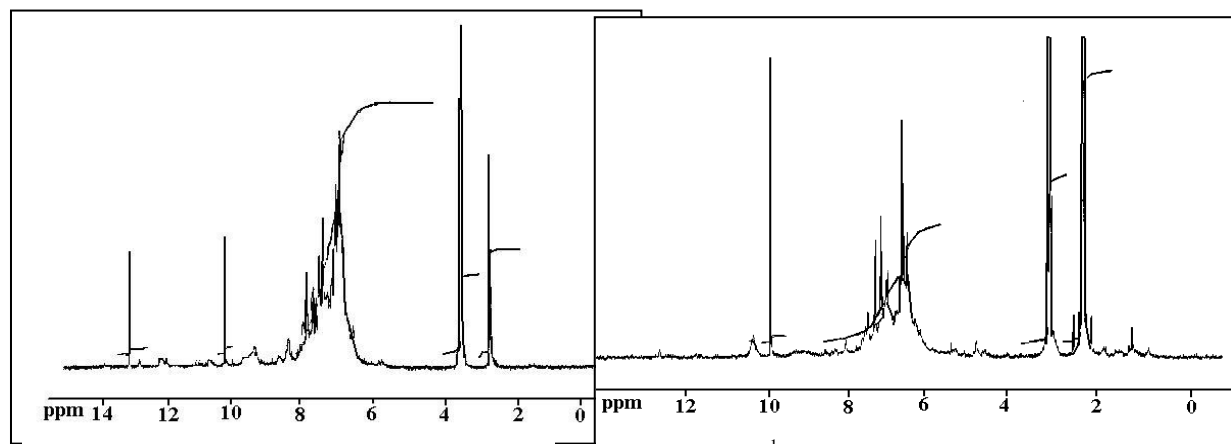


From the weak fields up to the higher ones, the A1 spectrum (Fig.3) exhibits 6 main chemical shifts in a ratio of the intensities 1:1:1:4:4:8.

The structure of adduct A2 can be explained if it is assumed that the proportion of the nitrile ligand (HL^6) is twice greater than that of the oxime and salicylaldehyde (HL^5), respectively. The intensity ratio mentioned in Table III and extracted from the NMR spectrum of A2 (Fig.4), corroborate the hypothesis that the hydrolyzed nitrile species and the oxime form present within the complex are in equal proportions.

Table III: ^1H NMR data for complexes A1 and A2 in DMSO (ppm).

Compounds	ppm (integration)	Assignment
Adduct A1	8-7.5 (8 protons)	(HL^5)
	7.5-6 (4 protons)	(HL^6)
	12.2 (1 proton)	H_1 (HL^5)
Adduct A2	13 (1 protons)	H_1 (HL^6)
	10.2 (1 protons)	H_1 (HL^5)
	8.3 (1 proton)	H_1 (H_2L^2)
	8-7.5 (8 protons)	(HL^6)
	7.5-7 (4 protons)	(HL^5)
	7-6 .5 (4 protons)	(H_2L^2)

Figure.3 ^1H NMR spectrum of A1Figure.4: ^1H NMR spectrum of A2.

The ^{51}V NMR spectrum for the polymeric adducts A2 in the solid state (Fig.5) shows three resonances at:

$\delta = -418$ ppm: 2 vanadium atoms bonded to triply-bridged oxygen atoms.

$\delta = -480$ ppm: 4 vanadium atoms bonded to doubly-bridged oxygen atoms.

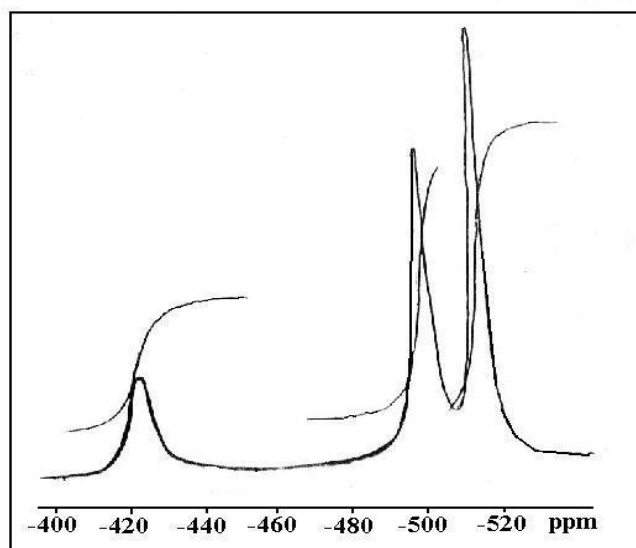
$\delta = -500$ ppm: 4 vanadium atoms bonded to terminal oxygen atoms.

These signals are in the range reported for the vanadium atoms in a decavanadate unit [2-8-9] and confirm the presence of three types of non-equivalent vanadium atoms.

The interaction of decavanadate with ligands is due to intermolecular hydrogen bonding established between the most acidic hydrogen ligand and the doubly and triply bridging oxygen atoms of $[\text{V}_{10}\text{O}_{28}]^{6-}$.

This polynuclear structure is clearly specified by the mass spectrometry study. The spectra of complexes show molecular peaks " $M + 1$ " = 1530 g/mol for A2 and 1526 g/mol to A2.

The NMR spectra of these same systems, carried out in CDCl_3 and DMSO, also revealed the presence of three resonance lines specific to decavanadate ion suggesting the maintenance of such structure in solution.

Figure.5: ^{51}V NMR spectrum of A2.

A1 and A2 compounds are adducts with mixed valences V(IV) -V (V) as confirmed by the electronic absorption spectrum of A2 given as example (Fig.6).

The electronic absorption spectra of A1 and A2 show two d-d transitions located around 450 nm ($\epsilon = 262 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) and 750 nm ($\epsilon = 401 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) and an intervalence band at 1075 nm ($\epsilon = 580 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$). The shoulder around 250 nm is attributed to the intra ligand $\pi \rightarrow \pi^*$ transition.

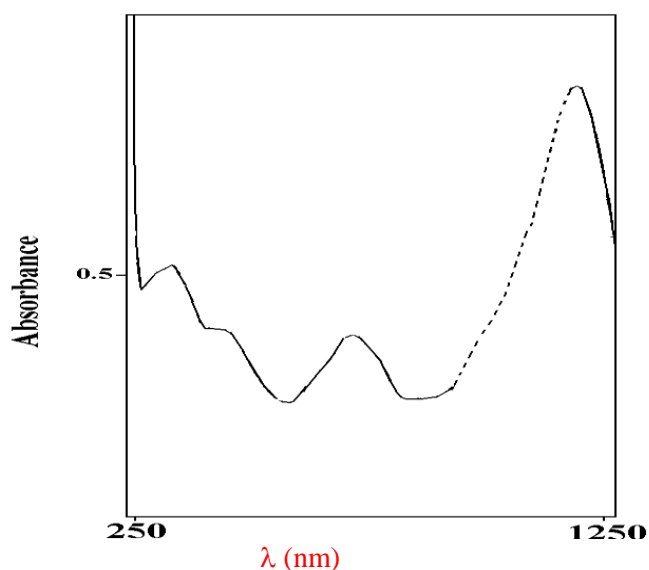


Figure.6: UV-visible spectrum of adducts in DMF.

The curves of EPR experience, performed at 300 K on A1 and A2 polycrystalline samples with respective magnetic moments 1.67 and 2.5 μB , are characteristics of compounds with a strong antiferromagnetic coupling between d^1 sites [9-12]. They show an isotropic single.

The analysis of the isotype resonance curves of A1 and A2 (Fig.7) allows us to determine the spectroscopic parameter g value which is 1.940. This value supports the idea of the establishment of a strong exchange interaction. This interpretation is supported by the appearance, in the central portion of the spectrum, of a Lorentzian shape that ends by a Gaussian one. Such situation is specific of an exchange interaction.

At liquid nitrogen temperature and still in the solid state, the shape of the curve is maintained with a slight increase of Lande factor. In both cases, the difference between g values and that of the free electron g (2.0023), indicate the importance of spin-orbit coupling.

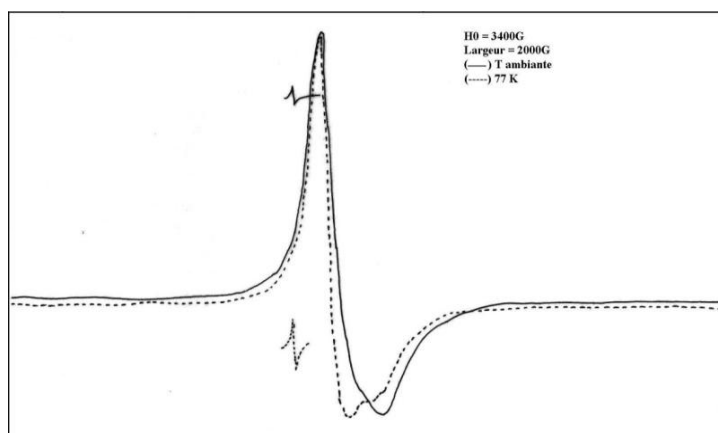


Figure.7: EPR spectrum of A1.

Each of the voltammograms of A1 and A2 presents three well-resolved reductions. The peaks are characterizing the reduction of three carbon vanadium (IV) around -0.45, -0.7 and -0.98 V / SCE. Each peak is involving a single electron transfer [9-13]. Only one anodic signal at -0.9 V / ESC appears on voltammograms.

4.2.Characterization of complexe C1

The elemental analysis and physical characterization, suggest that the trimer $[V^{IV}_2V^VO_5(HL^6)_3(L^6)_3(H_2L^1)_3] \cdot H_2O$ is formed.



Its IR spectrum (Fig.8) clearly reveals the dehydration of the oxime HL^6 by the presence of new vibrations at 2095 and 2229 cm^{-1} , characteristic of coordinated and free nitril groups. Furthermore, new bands appearing at 980 and 972 cm^{-1} are attributable to the stretching vibration of $V=O$, stronger than that of $V-O-V$, situated at 870 cm^{-1} in the spectrum of C1. In the region of ligand-metal vibrations, the three bands observed at 520, 500 and 420 cm^{-1} are assigned respectively to $\nu(V-N)$, $\nu(V-O)$ and $\nu(V-N(=C))$ [9-13]. Finally, a new wide band in the range 4000-3000 cm^{-1} , corresponding to an intramolecular $\nu(OH)$ band, and that at about 1606 cm^{-1} could be ascribed to a strong hydrogen bonding vibration.

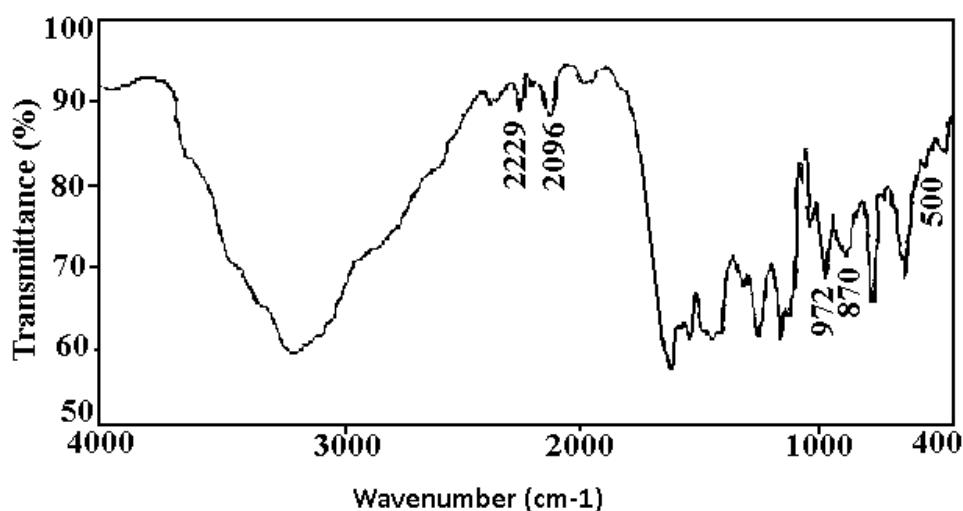
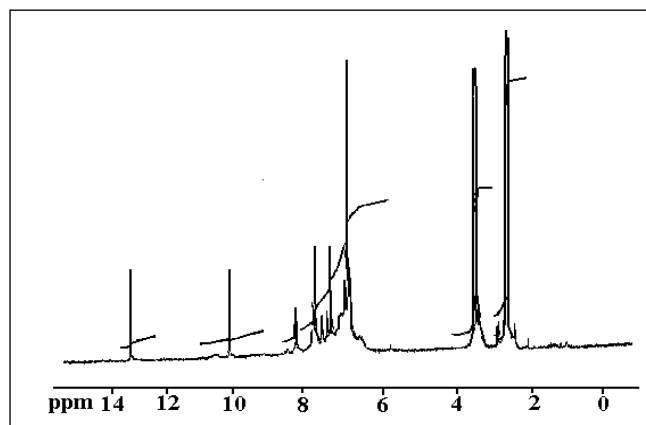


Figure.8: FTIR spectrum of C1 in KBr pellet.

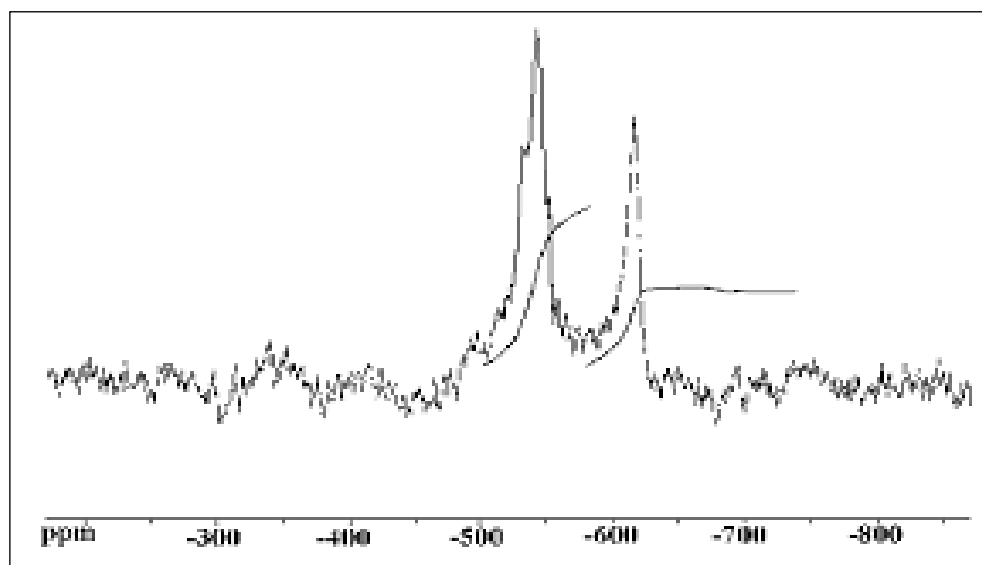
The proton resonances (Fig.9) of the phenyl groups in the ratio 1:1:1:4:8 resonate between 6.5-8 ppm. They correspond to the protons of the two nitrile ligands (HL^6 and L^6) and H_2L^1 ligand present in the coordination sphere of each vanadium ion. These results seem in agreement with IR deductions. The singlet at 13.5 ppm is due to the resonance of a strong hydrogen bond within this complex. This result is corroborated by the IR study concerning the vibration bond at 1606 cm^{-1} . The hydroxyl oximic protons and those in α position of the same function, appear, respectively, as singlets at 10.3 and 8.5 ppm. This result can be ascribed to the coordination of H_2L^1 to each metallic center.

Figure.9: ^1H NMR spectrum of C1.

The presence of d^0 and d^1 configurations within the complex is clearly determined by ^{51}V NMR spectrum.

The ^{51}V NMR spectrum of the complex exhibits two isotopic chemical shifts at -538.3 ppm (2 vanadium atoms) and -612.11 ppm (1 vanadium atom). They are associated, respectively; to the degrees V and IV of vanadium (Fig.10).

The data provided by the ^{51}V spectra in the deuterated DMSO and CDCl_3 , show the absence of the magnetic coupling between vanadyl and vanadic ions.

Figure.10: ^{51}V NMR spectrum of C1.

The electronic absorption of the complex C1 (Fig.11) is composed by a shoulder at $\lambda = 275$ nm ($\epsilon = 108.10^4 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) corresponding to the ligand \rightarrow metal charge transfer transition and two d-d transition $d_{xy} \rightarrow d_{xz}$, d_{yz} ($\lambda = 487$ nm, $\epsilon = 289.66 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) and $d_{xy} \rightarrow d_{x^2-y^2}$ ($\lambda = 681$ nm, $\epsilon = 128.28 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) which confirmed the presence of a d^1 system in C^4 symmetry. While the strong absorption around 1100 nm ($\epsilon = 1340 \text{ M}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) belongs to an intervalence $\text{V}^{\text{IV}} \rightarrow \text{V}^{\text{V}}$ transition which confers to C1 a bidental character [14].

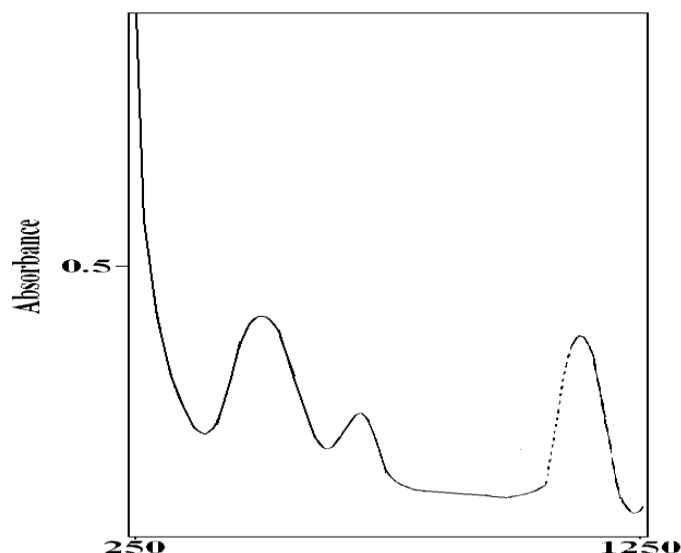


Figure.11: UV-visible spectrum of C1

In the solid state, the ERP study, realized at 300 and 77K (Fig. 12) is consistent with an isotropic structure with axial symmetry. Two parameters are accessible to measurements, it is about $g_{\parallel} = 1.930$, $g_{\perp} = 1.95$, where $g = 1/3 g_{\parallel} + 2/3 g_{\perp}$. These results indicate that the signal is due to a complex in a tetragonal environment, and the localization of the lone electron on the $3d_{xy}$ orbital ($g_{\parallel} < g_{\perp}$).

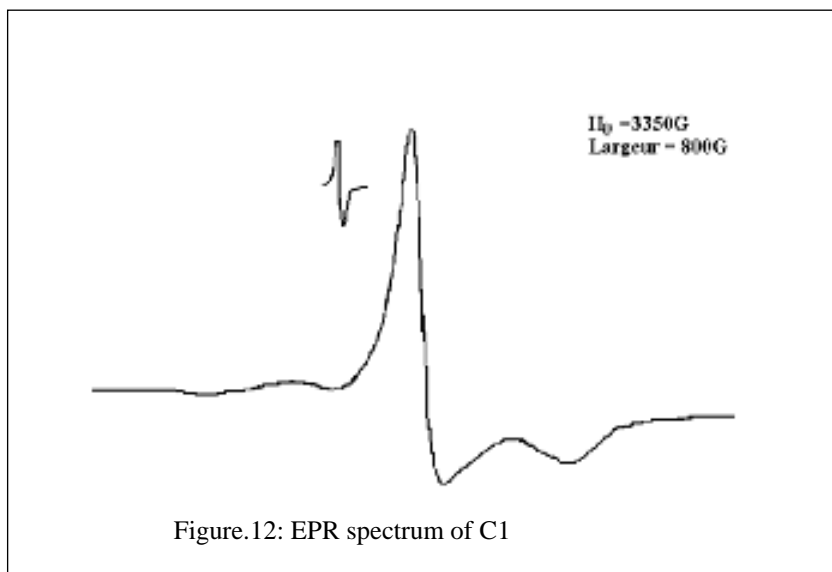
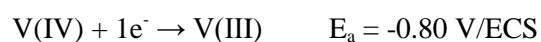
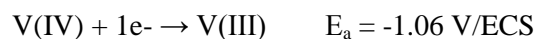


Figure.12: EPR spectrum of C1

The voltamogram of Complex C1 provides two mono-electronic steps corresponding to the couple V(IV)/V(III) (Fig.13). The two anodic waves involving the one electron confirm the reversibility of the system. The various peaks may be attributed, respectively to:



$$E_c = -0.85 \text{ V/ECS}$$



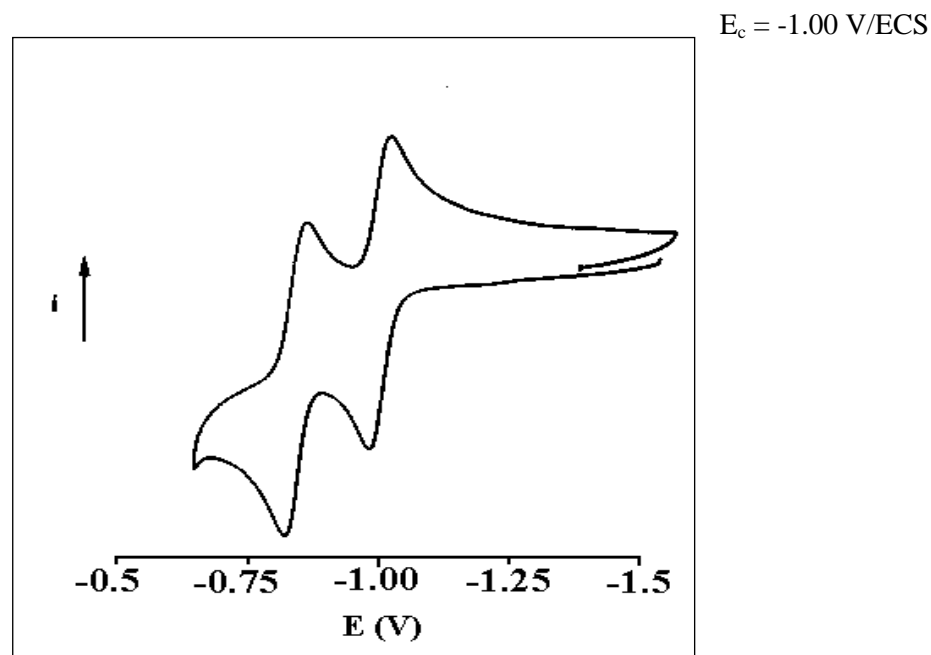


Figure.13: Voltammogram of complex C1

CONCLUSION

This work focused on synthesis of coordination compounds using hydrothermal synthesis method, under different experimental conditions. A correlation between the operating conditions of their synthesis and the structural evolution of the oxime has been established.

We have succeeded in preparing a series of new decanuclear clusters with satisfactory yields. The peculiarity of these compound is due to the exclusive presence of paramagnetic centers d^1 of vanadium.

The hydration and hydrolysis reaction of salicylaldoxime has been identified, leading to the formation of nitrile and carbonyl ligands in the immediate environment of vanadyl ions.

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