

Synthesis, Thermal and Electrical Studies on Solvated Oxovanadium(IV) Complexes with Schiff Bases Derived from Aromatic Diamines and 2-Hydroxy-1-naphthaldehyde

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Summary. Solvated oxovanadium(IV) complexes of Schiff bases derived from aromatic diamines and 2-hydroxy-1-naphthaldehyde have been prepared from ethanolic medium. The elemental analyses reveal that the complexes have the ratio 1:1, 2:2 and 1:2 (ligand:metal) composition which are nonelectrolyte in *DMF*. The coordination number six (octahedral geometry) is proposed for the complexes prepared. This is based on the results of IR, electronic and EPR spectra. TGA as well as DTA studies and the electrical properties and (*I-V*) characteristics for the metal complexes were investigated.

Keywords. Solvated oxovanadium complexes; Conductivity.

Synthese und thermische bzw. elektrochemische Untersuchungen an solvatisierten Oxovanadium(IV)-Komplexen mit Schiff-Basen aus aromatischen Diaminen und 2-Hydroxy-1-naphthaldehyd

Zusammenfassung. Die im Titel genannten Komplexe wurden in ethanolischem Medium hergestellt. Sie sind in *DMF* Nichtelektrolyte und haben laut Elementaranalyse die Zusammensetzung Ligand:Metall = 1:1, 2:2 und 1:2. Basierend auf IR-, UV- und EPR-Spektren wird die Koordinationszahl 6 (oktahedrale Geometrie) vorgeschlagen. Es wurden TGA- und DTA-Studien durchgeführt und das elektrochemische Verhalten der Metallkomplexe untersucht.

Introduction

Vanadium has been known for some years to be an essential trace element in both plants and animals although its function is still unclear [1]. The discovery that vanadate is a potential inhibitor of (Na-K)-Atpase has originated considerable interest in several vanadium dependent physiological and biochemical effects which have evidence that the predominant valence of vanadium within the tissues and cell is the +4 state [2].

Reactive complexes of vanadium IV, III and II states, that can be used as model compounds for studying the chemical reactivity of metal ion, were limited to

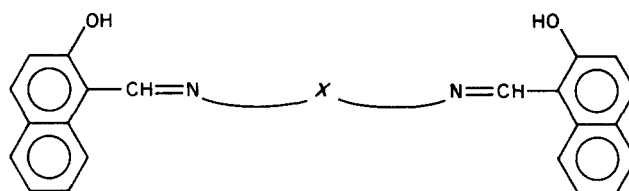
cyclopentadienyl derivatives [3]. Many different ligands have been used to form complexes with the VO^{+2} ion, but the ion's stability and lack of reactivity make these complexes virtually useless for studies of chemical reactivity at the metal site [4].

Oxovanadium salicylidene imine complexes are green and their spectral and magnetic properties indicated a tetragonal pyramidal structure [5]. Similar complexes involving derivatives of salicylaldehyde and trimethylene diamines were found to be polymeric in nature and have yellow to orange colour [6]. A square pyramidal geometry has often been assumed for five coordinated oxovanadium complexes [7].

In the present study a series of oxovanadium complexes with Schiff bases derived from aromatic diamines and 2-hydroxy-1-naphthaldehyde are prepared and characterized. The thermal properties, electrical conductivity and current–voltage (I – V) behaviour of these complexes were also investigated.

Experimental Part

The ligands used in the present study were prepared according to the method described by Diehl and Hash [8]. The compounds obtained have the general structural formula



in which X is as follows (according to ligands I–VI):

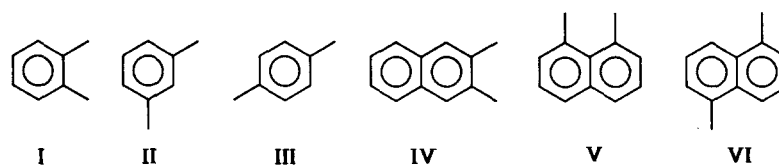


Table 1. Analytical data for the oxovanadium(IV) Schiff base complexes 1–6 (ligands I–VI)

No.	Complex	Microanalysis data: found (calc.)			
		% C	% H	% (N)	% V
1	$[\text{VO}(\text{EtOH})]\text{H}_2\text{O}$	65.0(66.0)	5.16(4.77)	5.1(5.13)	9.1(9.35)
2	$[(\text{VO})\text{L}(\text{EtOH})_2]4\text{H}_2\text{O}$	54.4(53.9)	5.4(5.3)	3.5(3.9)	13.9(14.3)
3	$[(\text{VO})\text{L}(\text{EtOH})_2]3\text{H}_2\text{O}$	65.2(66.0)	5.1(4.77)	5.7(5.14)	–
4	$[(\text{VO})\text{L}(\text{EtOH})]3\text{H}_2\text{O}$	65.0(64.6)	5.34(5.1)	4.6(4.4)	7.8(8.1)
5	$[(\text{VO})\text{L}(\text{EtOH})]5\text{H}_2\text{O}$	60.6(61.2)	5.14(5.5)	3.5(4.2)	7.3(7.65)
6	$[(\text{VO})\text{L}(\text{EtOH})]_22\text{H}_2\text{O}$	59.6(60.1)	5.34(4.9)	4.5(4.6)	–

The oxovanadium complexes of the Schiff bases were prepared according to the method reported previously [9]. The analytical data of the complexes are collected in Table 1.

The solid state IR spectra were recorded as KBr discs on the Perkin Elmer 598 Spectrophotometer. The electronic absorption spectra in *DMF* as a solvent were recorded on a Shimadzu 240 UV-Vis Spectrophotometer. The *x*-band EPR spectra were recorded on a Varian E₉ Spectrophotometer. The thermal analyses (TGA and DTA) were carried out on a Dupont 900 thermal analyzer; 10–16 mg of the sample was heated up to 750 °C, using a heating rate of 10 °C min⁻¹ in air. The electrical conductivity and the current–voltage (*I–V*) measurements were carried out using a Super Megohmmeter electrometer (Model 170) as described previously [10].

Results and Discussion

Elemental Analyses

The results of elemental analyses, Table 1, are generally in accordance with the composition suggested for the various complexes. This reveals that all complexes display almost similar interaction between the Schiff bases and oxovanadium ions.

IR Spectra

The IR-bands of diagnostic importance of the complexes are listed in Table 2 along with their tentative assignment. The following conclusions can be pointed out:

i) The solid state IR spectra of all complexes compared with those of ligands indicate that the $\nu_{\text{C=N}}$ band at 1628–1620 cm⁻¹ is shifted to lower values indicating that the ligands coordinated to the metal ions through nitrogen atom of the azomethine group and probably in the dianionic form [11].

ii) The ν_{OH} bands of the ligands are masked by the strong bands of water and ethanol. However, the bands due to δ_{OH} at 1345–1370 cm⁻¹ and $\nu_{\text{C-OH}}$ at 1240–1280 cm⁻¹ in the spectra of the ligands disappeared on complex formation supporting the displacement of protons from the phenolic groups through the metal ion.

iii) It is safe to assign the strong bands at 2520 and 960 cm⁻¹ to γ_{OH} of ethanol molecules and V=O stretching mode [12, 13]. Also, new bands at 577 and 485 cm⁻¹ are probably due to V–N and V-ethanol stretching modes.

The results of IR-spectra and elemental analyses denote that the Schiff base molecules behave as tetradentate dianionic ligands. For ligands I, IV, and V, the two azomethine nitrogens and the two phenolic oxygen atoms can be bonded to oxovanadium ion leading to stable three ring structures **1**, **4**, and **5**:

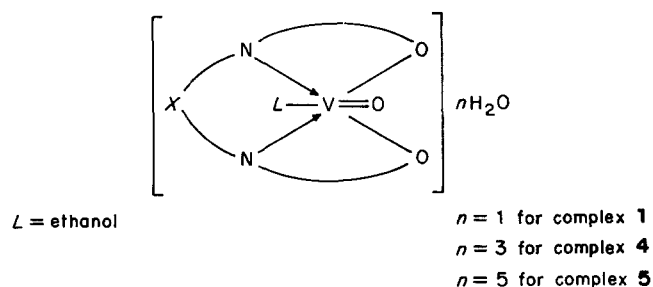
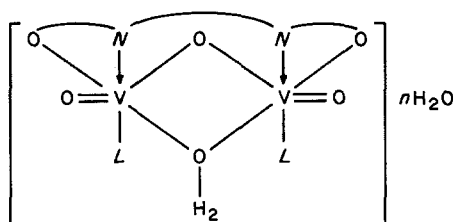


Table 2. Mass losses of some vanadyl Schiff base complexes

No.	% H ₂ O + Ethanol			% V ₂ O ₅		
	Temp. °C	Calc.	Found	Temp. °C	Calc.	Found
1	30–180	11.74	12.2	475–850	27.5	27.0
2	30–140	23.03	22.8	650–750	42.13	41.7
3	30–140	11.74	11.4	475–650	27.5	26.5
4	30–150	13.37	12.2	500–700	24.46	24.0

For ligands **II**, **III**, and **VI**, the two nitrogen atoms are so far apart that they cannot be bonded to one and the same oxovanadium ion. Hence, the Schiff base molecules in this case would be bonded to two metal ions behaving as monobasic bidentate ligand towards each oxovanadium ion.

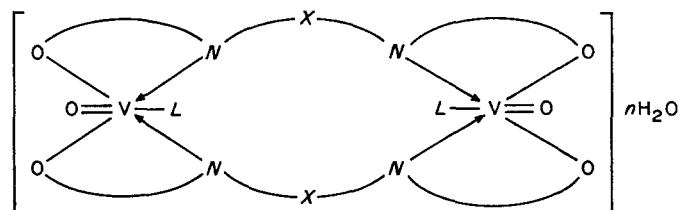
For ligand **II**, the bonding would lead essentially to a binuclear structure **2** due to steric effects:



$n=3$ for complex **2**

This is supported from the low solubility of the component in the different solvents and the high molecular weight.

For ligands **III** and **VI**, the bonding of the oxovanadium ion to two molecules of the Schiff base can lead to dimeric structures **3** and **6**:



$n=3$ for complex **3**

$n=2$ for complex **6**

L = ethanol

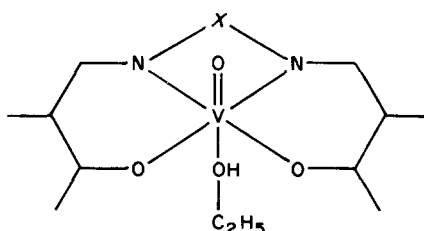
This dimeric form is analogous to other complexes of vanadium(IV) with almost similar ligands [14]. This view is supported by the unusually low V=O stretching frequency which results from mutual interactions between the two adjacent vanadium atoms. An identical behaviour was observed for oxovanadium complexes of Schiff bases derived from aliphatic diamines [9].

Electronic Spectra

The electronic absorption spectra of the oxovanadium Schiff base complexes were measured using the nujol mull technique. Although the assignments of the electronic spectra of the oxovanadium(IV) ion are still not agreed upon [7], the pattern of the absorption spectra can nevertheless be used to obtain information about the spatial distribution of the ligated groups around the V atom. The electronic spectra of the complexes are characterized by charge transfer bands at 450–430 nm and a weak shoulder at 550–530 nm which can be assigned to d-d transitions. From the data of the nujol mull spectra it can be pointed out that the VO (IV) complexes have a six coordinate pseudo octahedral structure [7, 15].

EPR Spectra

The solid state EPR spectra of the oxovanadium Schiff bases with ligands **I**, **IV**, and **V** exhibit a strong signal with $g_{\text{eff}} \approx 2$. The hyperfine coupling constants A_0 range from 86–117 for the three complexes. The g and A_0 values are within the range expected for the adduct VON_2O_2 chromophores and reveal that the A_0 values are a more sensitive measure for chelate formation [16] than g -values, the latter are characteristic of normal oxovanadium complexes [13]. The shape and position of the EPR signals are in favour of octahedral arrangement of the ligand around the central vanadium atom. Based on the data obtained, the oxovanadium complexes can be represented as follows:



The EPR spectra of the oxovanadium complex with ligands **II**, **III**, and **VI** show more broadening of the signals than for the mononuclear complexes which is probably due to association of the VO complexes in dimeric or polymeric structures.

Table 3. IR and electronic spectra of oxovanadium(IV) Schiff base complexes

No.	IR spectra (cm^{-1})						Electronic spectra (nm)		
	ν_{OH}	ν_{CH}	$\nu_{\text{C=N}}$	δ_{OH}	$\nu_{\text{C-OH}}$	$\nu_{\text{V=O}}$	L_b^{-1} A naph	CT	d-d
1	3400	2940	1610	1360	1280	960	340	440	540
2	3440	2930	1613	–	1270	970	320	430	550
3	3350	2870	1613	1345	1300	965	318	240	530
4	3380	2900	1612	1360	1240	965	350	448	550
5	3380	2890	1610	1370	1250	960	345	445	550
6	3390	3000	1618	–	1260	960	350	450	–

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The principal thermogravimetric data are collected in Table 3. The thermal decomposition of all complexes take place in three main stages which can be explained as follows:

i) The desolvation of the complex **1** (at 30–200 °C) takes place in two steps, the first one is due to the removal of hydration water and the second step corresponds to the elimination of the coordinated ethanol molecule.

ii) The anhydrous complex is stable up to 230 °C, the thermal stability of the chelate can be referred to the formation of the six membered ring structure around the metal ion. Further heating leads to a partial degradation of the complex.

iii) Complete decomposition of the organic residue and the formation of the oxide V_2O_5 as a final degradation product is achieved at 600 °C.

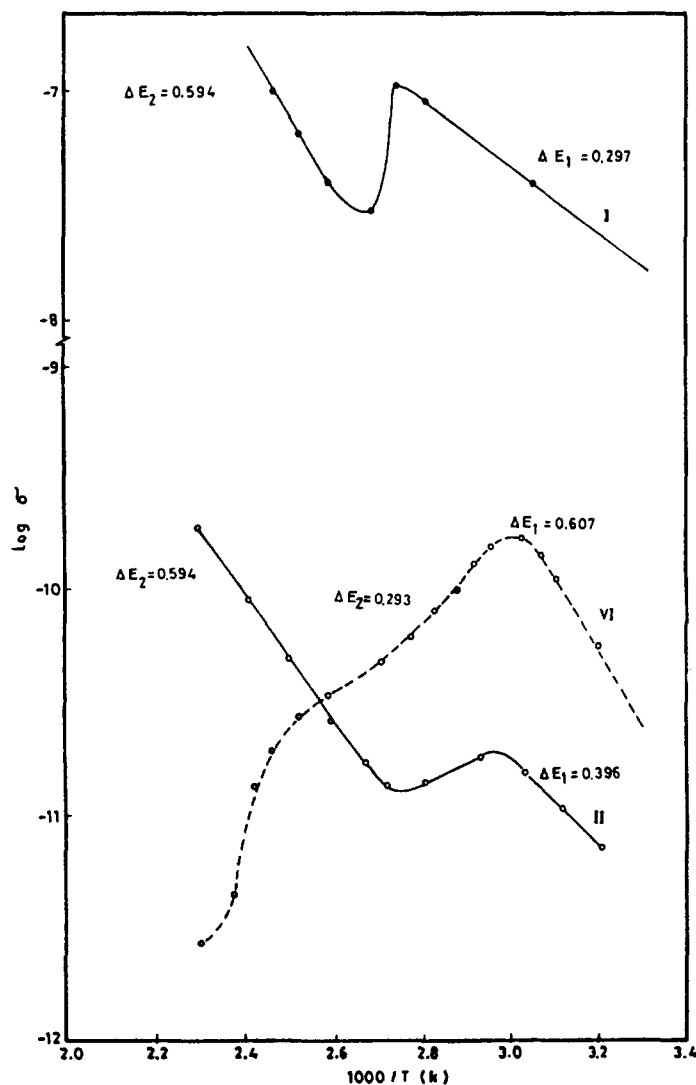
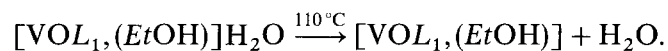


Fig. 1. The variation of $\log \sigma$ versus $1/T [K^{-1}]$ of the complexes **1**, **2**, and **6** (ligands **I**, **II**, and **VI**)

The interpretation of the DTA curves for the complexes presents a number of problems. These problems are similar to those found for the metal salt hydrate systems [17, 18] in which endothermic peaks were found which can be caused by reactions of the type:



The investigated complexes show endothermic peaks in the 90–135 °C temperature range. These peaks are assigned to the removal of hydration water and coordinated ethanol [19]. The exothermic peaks at 180 and 210 °C, 360 °C, and 400 °C and finally at 510 °C for complex 1 are attributed to irreversible thermochromism, melting, vaporization and finally decomposition.

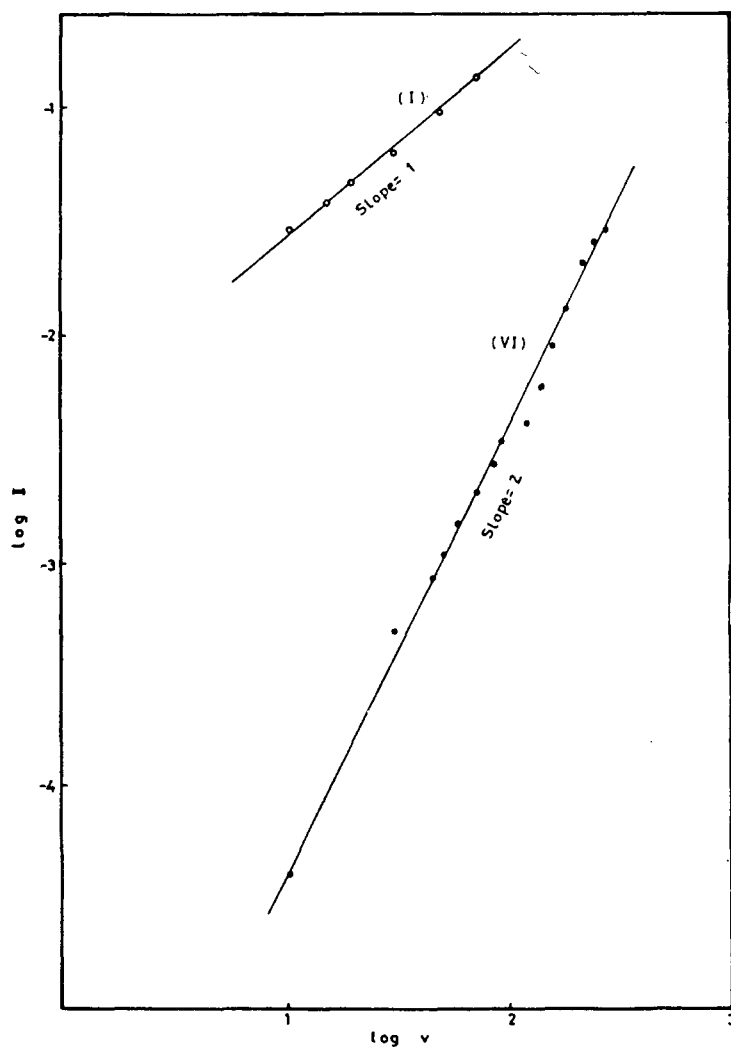


Fig. 2. The (*I*-*V*) characteristics on a log-log plot for complexes 1 and 6 (of ligands I and VI)

Electrical Conductivity

The electrical conductivity of the complexes **1**, **2** and **6** was measured as a function of temperature. Figure 1 shows the plots of $\log \sigma$ versus the reciprocal absolute temperature ($1000/T$) according to the equation

$$\sigma = \sigma_0 \exp(-\Delta E/kT),$$

where σ_0 is a constant (pre-exponential factor), ΔE is the activation energy and k is the Boltzmann constant. It can be shown that there is a positive coefficient of the electrical conductivity ($d\sigma/dT$) for the complexes **1**, **2** and **6** from room temperature up to 90, 63, and 55 °C, respectively. Therefore, in these ranges the complexes have semiconducting properties. However, a metallic behavior was observed in the temperature range (90–110 °C), (63–90 °C) and (55–120 °C) for the three complexes. This can be attributed to the loss of water molecules from the complexes during the dehydration process. The inflection temperature between the metallic and semi-conducting behavior coincides with the dehydration process.

The deduced ΔE values at the semiconducting range are 0.297, 0.396, and 0.607 eV for complexes **1**, **2** and **6**. These values are highly dependent on the molecular structure of the complexes and the nature of the organic portion of the ligand. The highest value for complex **6** could be attributed to the replacement of the two hydrogen atoms by two VO^{++} ion. This may cause a distortion in the conduction pathways between the metal and ligand, hence decreases the electron migration [20].

The I – V characteristic on log-log plot for complexes **1** and **6**, Fig. 2, indicate that the proportionality of I to V^n with $n = 1$ and 2, respectively. This reveals that complex **1** obeys Ohm's law but complex **6** proceeds via space charge limiting current (SCLC).

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