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Polymer complexes. LVIII. Structures of supramolecular assemblies of vanadium with chelating groups

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ABSTRACT

Oxovanadium(IV) polymer complexes of formulation {[(VO)L]₂_n (1) and [(VO)LB]_n (2–4), where H₂L is tridentate and dianionic ligand (allylazorhodanine) and B is planar heterocyclic and aliphatic base have been prepared and characterized by elemental analyses, IR, ¹H NMR, electronic spin resonance spectra, magnetic susceptibility measurements, molar conductance and thermal studies. The molecular structure shows the presence of a vanadyl group in six-coordinate VNO₃/VN₃O₃ coordination geometry. The N,N-donor heterocyclic and aliphatic bas displays a chelating mode of binding with an N-donor site trans to the vanadyl oxo-group. In all polymeric complexes (1–4) the ligand coordinates through oxygen of phenolic/enolic and azodye nitrogen. The molar conductivity data show them to be non-electrolytes. All the polymer complexes are ESR active due to the presence of an unpaired electron. The calculated bonding parameters indicate that in-plane σ bonding is more covalent than in-plane π bonding. From the electronic, magnetic and ESR spectral data suggest that all the oxovanadium(IV) polymer complexes have distorted octahedral geometry. The thermal decomposition process of the polymeric complexes involves three decomposition steps.

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1. Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups and it is multiplied manifold when the ligands have biological importance [1]. The number and diversity of nitrogen, oxygen and sulfur chelating agents used to prepare new coordination and organometallic compounds has increased rapidly during the past few years [2–4].

The coordination chemistry and biochemistry of allyl heterocyclic have attracted increased interest due to their chelating ability and their pharmacological application [1]. The pharmacological activity is found to be more in the case of metal polymer complexes when compared to the free ligand, and some side effects may decrease upon complexation [5].

The chemistry of vanadium has received considerable attention due to the discovery that vanadium is an essential element in biological system. Schiff base and related vanadium complexes have important application in biology and medicine [6] as well as in the catalysis associated with chemical and petrochemical processes [7], also act as inhibitors of enzymes [8] and antifungal/antibacterial agents [9].

The potential catalytic abilities of vanadium compounds have lead to an increasing interest in vanadium coordination chemistry in recent years [10]. Coordination polymers i.e. polymeric metal complexes derived from simple or polymeric coordination ligands are generally insoluble in common solvents and added advantage, over monomer analogues, of easy separation from the catalytic reaction mixture leading to operational flexibility and recyclability [11,12]. Synthesis and structural studies of a interesting series of heterocyclic adducts of oxovanadium(IV) complexes of some arovlhydrazones have been reported [13]. Vanadium(IV) complexes containing SNO donor sets have also been reported [14]. In the case of oxovanadium complexes, monomeric and five coordinated oxovanadium(IV) complexes are formed with several bidentate Schiff bases, but dimeric and five or six coordinated are formed with tridentate Schiff bases [15]. Recently reported oxovanadium(IV) based coordination polymers by Ando et al. [16] are insoluble in common solvents and their catalytic oxidation reactions are heterogeneous in nature [16]. The objective of the present work is to synthesis, spectral and ESR investigations of some polymeric oxovanadium(IV) complexes with different ONO donor ligand derived from allylazorhodanine. Heterocyclic and aliphatic bases viz. 2,2'bipyridine (bipy), pyridine (py) and ethylenediamine (en) were used as auxiliary ligands for coordination. .

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Fig. 1. The structure of azodye (H₂L).

2. Experimental

All reagents used for the preparation of the ligand and polymer complexes were of analytical grade.

2.1. Reagents

2-Aminophenol and Allyl rhodanine (Aldrich Chemical Co. Inc.) were used without further purification.

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co. Inc.) was purified by dissolving in hot ethanol and filtering [17]. The solution was left to cool. The pure material then being collected by filtration and dried.

2.2. Preparation of the

3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(o.hydroxyl phenyl)] (H₂L) monomer

The ligand H₂L (Fig. 1) was prepared and purified according to El-Sonbati School [18-22]. Monomer (H₂L) was typically prepared by adding a 25 mL of distilled water containing hydrochloric acid (12 M, 2.68 mL, 32.19 mmol) to allyl rhodanine (10.73 mmol). To the resulting mixture, stirred and cooled to 0°C, a solution of sodium nitrite (10.73 mmol, in 20 mL of water) was added drop wise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution (2-aminophenol) (10.73 mmol) in 20 mL of ethanol containing 602 mg (10.73 mmol) of potassium hydroxide. The red precipitate, which formed immediately was filtered and washed several times with water. The crude product obtained was purified by crystallization from hot ethanol (yield \sim 65%). The analytical data confirmed by expected composition. Found: C, 49.22; H, 3.88; N, 14.05; S, 21.55%; C₁₂ H₁₁N₃O₂S₂, Cal. C, 49.15; H, 3.75; N, 14.35; S, 21.84%. The ligand was also characterized by ¹H NMR and IR spectroscopy. The IR spectrum of the monomer showed the presence of an N=N (1485) and OH (3330) cm^{-1} . ¹H NMR (300 MHz, DMSO- d_6): δ (ppm) ~12.8 (OH); 6.25, 5.12 $(CH_2=CH).$

2.3. Preparation of poly {3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(o.hydroxyl phenyl)] (PH₂L) homopolymer

PH₂L homopolymer was prepared by free radical initiation of H₂L using 0.1% (w/v) AIBN as initiator and DMF as solvent for ~7 h. The polymer product was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40 °C. The PH₂L homopolymer has been characterized by IR, ¹H NMR. The inherent viscosity ($\eta_{inh} = \ln_{r/c'}$, C = 0.49 g/dl), measured in a Desreux–Bishoff suspended level viscometer at 30±0.01 °C, using chloroform as solvent is $\eta_{inh} = 1.24$.

2.4. Synthesis of the solid polymer complexes

Method A: The VO(IV) chelates with H_2L was prepared by refluxing VOSO₄·5H₂O(0.001 mole) with the corresponding ligand (0.001 mole) in 20 ml DMF as a solvent, and 0.1% (w/v) AIBN as initiator were used. The resulting mixture was heated at reflux for 4 h (Fig. 2). The hot solution was precipitated by adding a large excesses of distilled water, containing dilute hydrochloric acid, to remove the metal salts that were incorporated into the polymer complexes.



Fig. 2. Tentative structure of polymer complex $\{[VOL]_2\}_n$ (1).

Analytical data of the polymer complexes (for molecular structure see Figs. 1 and 4).

Complex ^a	Method of Preparation ^b	Experimental (Calcd.) %					
No.		С	Н	N	S ^c metal	Molar ratio	
$\{[(VO)L]_2\}_n$ 1	А	40.34 (40.23)	2.40 (2.51)	11.87 (11.73)	!8.12 14.51 (17.88)(14.23)	1:1	
[(VO)L.Py] _n 2	В	46.80 (46.69)	3.32 (3.21)	13.05 (12.82)	14.84 11.85 (14.65) (11.66)	1:1:1	
[(VO)L.en] _n 3	В	40.08 (40.20)	4.22 (4.07)	17.01 (16.75)	15.05 12.37 (15.31) (12.19)	1:1:1	
[(VO)Lbipy] _n 4	В	51.50 (51.37)	3.42 (3.31)	13.62 (13.80)	12.71 10.30 (12.45)(9.91)	1:1:1	

^a H₂L is the ligand as given in Fig. 1 and L is the anion; air-stable; no-hygroscopic.

^b See text.

^c Estimated gravimetrically.

The polymer complex (1) (see Table 1) was filtered, washed with water, and dried in a vacuum oven at $40 \degree C$ for several days.

Method B: The polymer complexes (**2–4**) were prepared from a general synthetic procedure in which the ligand (0.001 mole) in DMF (15 ml) was reacted with VOSO₄·5H₂O (0.001 mole) in 10 ml DMF. The resulting mixture was stirred 30 min to obtain a homogeneous and clear solution that was subsequently reacted with the corresponding heterocyclic base (Py/en/bipy) (0.001 mol) taken in 10 ml DMF as a solvent, and 0.1% (w/v) AIBN as initiator were used. The resulting mixture was heated at reflux for 4 h (Fig. 3). The hot solution was precipitated by adding a large excesses of distilled water, containing dilute hydrochloric acid, to remove the metal salts that were incorporated into the polymer complexes. The polymer complexes were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days.

2.5. Measurements

C, H, and N microanalyses were carried out at the Cairo University Analytical Center, Egypt. ¹H NMR spectrum was obtained with a Jeol FX90 Fourier transform spectrometer with DMSO- d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded using Perkin-Elmer 1340 spectrophotometer. Ultraviolet-Visible (UV-Vis) spectra of the polymer were recorded in nuzol solution using a Unicam SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy method. Mercury(II) (tetrathiocyanato)cobalt(II), [Hg{Co(SCN)₄}], was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [23] and Pascal's constants. Magnetic moments were calculated using the equation, $(_{eff.} = 2.84 [T(_{M}^{coor.})^{1/2}]$. EPR measurements of powdered samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenylpicrylhydrazyle (DPPH) as a reference material. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10°C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, $10 \text{ mm} \times 5 \text{ mm} \times 2.5 \text{ mm}$ deep; the temperature measuring thermocouple was placed within 1 mm of the holder.



Fig. 3. Ternary structures of [VOLB]_n (2-4) and the bases (B) used.

3. Results and discussion

3.1. General

The azo group can act as a proton acceptor in hydrogen bonds [18,19]. The role of hydrogen bonding in azo aggregation has been accepted for some time. Intramolecular hydrogen bonds involving o.OH or o.COOH groups with the -N=N- group increased their stabilities through chelate ring structure [18,24]. The strength of the hydrogen bond of o.hydroxyazo compounds depends on the nature of substituents present in the coupling component from the aryl azo group. Chelating rings formed by NH...N bonds are less stable than corresponding rings formed by OH...N bonds [25]. The U.V. spectra of acetylaminoazobenzene showed that the chelate ring is stable in dioxan and in methanol solvents, whereas the chelate ring in 2-hydroxy-4-methylazobenzene is stable in dioxan and hydroxylic solvents. Chelate rings involving NH...N=N bonds in azo compounds (e.g. 2-amino-4-dimethylaminoazobenzene) have been treated theoretically and have been studied in the IR and UV spectra where both five and six membered chelate rings with NH...N bonds have been suggested [26]. The attachment of the OH group to o- or p-position increase the acidity, for example 1-phenylazo-2-naphthol, was found to be stronger than in the 2-hydroxyazobenzene forming intramolecular hydrogen bond leading to a larger resonance system [27].

In general, most of the azo compounds give spectral localized bands in the wavelength range 47,620–34,480 and 31,250–27,000 cm⁻¹. The first region is due to the absorption of the aromatic ring compared to ${}^{1}B_{b}$ and ${}^{1}L_{b}$ of mono substituted benzene and the second region is due to the conjugation between the azo group and the aromatic nuclei with intermolecular charge transfer resulting from π -electron migration to the diazo group from electron donating substituents.

3.2. Synthesis and general properties

Oxovanadium(IV) polymer complexes of formulation $\{[(VO)L]_2\}_n$ (1) and $[(VO)L.B]_n$ (2–4), where H_2L is tridentate and dianionic ligand (allylazorhodanine) and B is planar heterocyclic and aliphatic base (bipy; py; en), are prepared in high yield from a general synthetic procedure in which vanadyl sulphate is reacted with the azodye and B in DMF. The results of elemental analysis of the mixed ligand and polymer complexes are in good agreement with those required by the proposed formula (Figs. 2 and 3). Selected physicochemical data are given in Table 1. The non-electrolytic complexes are soluble in DMF and DMSO. They show characteristic vanadyl (V=O) and azonitrogen (-N=N-) infrared bands at 750 and 1485 cm⁻¹, respectively. The polymer complexes are one-electron paramagnetic giving a magnetic moment value of ~1.60 B.M.

3.3. Elemental analyses of the polymer complexes

Analytical data indicated that the diazo coupling reaction between 2-aminophenol and allyl rhodanine occurred in 1:1 molar ratio and the product formed well defined polymer complexes with vanadium sulphate. The generalized equation for the reaction leading to the formation of the polymeric complexes is shown as follows:

 $VOSO_4 \cdot 5H_2O + H_2L \rightarrow \{[VOL]_2\}_n + H_2SO_4$

 $VOSO_4 \cdot 5H_2O + H_2L + B \rightarrow [VOLB]_n + H_2SO_4$

Formation of the polymer complexes has been done on the basis of their elemental analytical data, molar conductance values and magnetic susceptibility data. All the complexes show $1:1\{[VOL]_2\}_n/1:1:1[VOLB]_n$ metal:ligand/metal:ligand:base stoichiometry. They are non-hygroscopic, decompose and possess good keeping qualities. All the polymer complexes are insoluble in common organic solvents except DMF and DMSO. The molar conductance values in DMSO reveal the non-electrolytic nature of the metal complexes [28].

3.4. ¹H NMR spectrum

The ¹H NMR spectrum of ligand show two singlets corresponding to phenolic –OH and –NH. The singlet at $\delta = \sim 12.8$ ppm and $\delta = \sim 10.9$ ppm represent –OH and –NH, respectively of the formation of intramolecular hydrogen bonding with azonitrogen. The ligand do not show any peak attributed to enolic–OH proton indicating that they exist in keto form. Upon addition of D₂O the intensities of both OH and NH protons significant decrease. Further, the CH signal vanish and a new NH signal appear i.e., change from azo to hydrazone form (Fig. 4). This supports the assignment. The protons of the aromatic ring resonate downfield in the δ 7.3–8.4 ppm range.

The NMR spectrum of H₂L monomer showed the expected peaks and pattern of the vinyl group (CH₂=CH), δ 6.25 ppm (dd, *J* = 17, 11 Hz) for the vinyl CH proton and proton δ 5.12 ppm (AM part of AMX system dd, *J* = 17, 1 Hz) for the vinyl CH₂ protons, respectively. These peaks disappeared on polymerization while a triplet at δ 1.86 (t, *J* = 7 Hz) and a doublet at 1.80 ppm (d, *J* = 7 Hz) appeared, indicating that the polymerization of H₂L monomer occurs on the vinyl group [4,27]. It is worth noting that the rest of the proton spectrum of the monomer and polymer remain almost without change.

3.5. Infrared spectra

The structural elucidation of the polymer complexes is also supports by IR spectra and comparison of IR spectrum of the ligand (H₂L) with those of isolated metal complexes indicate the mode of bonding. The infrared spectrum of ligand exhibit strong to medium broad bands in the frequency ~3325 cm⁻¹. These bands can be attributed to intramolecular hydrogen bonded –OH group [18,29,30]. Furthermore, ligand exhibit a strong band due to C=O [18,29,30]. The discussed infrared features beside the band appeared at ~1615 cm⁻¹ can guide to assume the presence of C=N structure through resonating phenomena [24]. Such class of compounds is with different types of hydrogen bonding [29,30].

- i) H-bonding of the type O-H...N between the –OH group and –N=N– group (Fig. 4-C₁ & 4-C₂).
- ii) H-bonding of the type N-H...O between the -NH group and C=O group (Fig. 4-D).
- iii) Intermolecular hydrogen bonding of the O-H...N (Fig. 4-E) or N-H...O (Fig. 4-F) type of one molecule to another one.

a	bl	e	2	

Electronic spectral assignments (cm⁻¹) of oxovanadium(IV) Polymer complexes.

Species ^a	Intraligand transition	LMCT	d-d
H ₂ L	26250, 30674, 33550, 39470	-	-
1	36355, 30300	26173	18378
2	34700, 31685	25775	18278
3	34010, 31750	27115	17540
4	34000, 31745	27115	18265

^a See Table 1.

iv) The intramolecular hydrogen bonds in *o*.OH group with –N=N– group increased their stabilities through chelate ring structure [24]. Thus, the (i) case is more favoured than (ii).

The following features for some of the prepared polymer complexes are observed:

- i) The infrared spectra of the free ligands show no characteristic absorption assignable to $\rm NH_2$ function. This confirms the formation of the azo compounds.
- ii) The ligand exhibit bands in ~1728, 3185 and 3325 cm⁻¹ due to C=O, N-H and O-H stretches, respectively. These bands are absent in polymeric complexes, which suggests deprotonation of the phenolic group indicating the coordination through phenolic oxygen, and enolisation of the carbonyl group, followed by deprotonation [31]. A new band appearing in the ~1285 \pm 5 cm⁻¹ in the polymer complexes was assigned to the υ (C-O) (enolate) mode [32].
- iii) The disappearance of the phenolic–OH group is an evidence for the ligand coordination around the metal ion in its deprotonated form [32]. This causes υ (C–O) to shift to lower frequencies and a new band in the range ~507 cm⁻¹, assigned to υ (V–O) is found in polymer complexes which confirm the coordination of the ligand *via* phenolic oxygen [31].
- iv) The shifting of (-N=N-) to lower wavenumbers in the metal polymeric complexes by 25–35 cm⁻¹ indicates the coordination of azo nitrogen to the metal. Furthermore, the bands in the regions 550–565 and 420–430 cm⁻¹ can be assigned to the stretching modes of the metal to ligand bonds, v(V-O) and v(V–N), respectively [33]. In addition, the compounds exhibit a strong band in the 955–965 cm⁻¹ range due to the terminal V=O stretching [34], indicates hexa-coordinated environment around the metal center (Fig. 3). Complex (1) has a band in the region 830 cm^{-1} indicating V–O–V bridge vibration [35]. Tentative structure of complex (1) is shown in Fig. 2. The frequency range observed in polymer complexes indicates that V=0 bond is weakened by strong σ and π electron donation by enolate and phenoxy groups to the antibonding orbital of the V=O group [36]. The variation in frequency suggests that the $d\pi$ $p\pi$ overlap between vanadium and oxygen atom is influenced by substituents and coligands [32].
- v) In the spectra of mixed bipy-polymeric complexes the bands of bipy-free ligand at 750 cm⁻¹ are shifted to higher frequency around 780 cm⁻¹ in the polymeric complexes. The spectra of mixed en-polymeric complexes show two characteristic band at 3235 and 3295 cm⁻¹ assigned to v_{sym} and v_{asym} vibration of NH₂ suggesting coordination through NH₂ [36]. Also, in compound (**2**) a new band appears in 1617 cm⁻¹, attributable to coordinated pyridine. Thus, the nitrogen of pyridine is coordinated to metal ion.

3.6. Electronic spectra

Electronic spectral data of the ligand and polymer complexes in DMF solution are summarized in Table 2. The ligand (H_2L)



Fig. 4. General formula and proton numbering of 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione[(2-aminophenol)] azodaye (H2L).

exhibits bands at 381 nm (CS) $(n \rightarrow \pi^*)$, 326 nm (CO) $(n \rightarrow \pi^*)$, 298 nm (H-bonding and association), 253 nm (phenyl) (ph-ph*, $\pi-\pi^*$) [18] and 340 nm transition of phenyl rings overlaped by composite broad $\pi-\pi^*$ of azo structure. In the VO(IV) complexes, the (CS) $(n-\pi^*)$ transition shifts slightly to lower energy and remain almost constant. The (CO) $(n \rightarrow \pi^*)$ transition disappears with the simultaneous appearance of a new bands (\cong 339 nm), being attributed to $\pi \rightarrow \pi^*$ (C=C) as a sequences of enolization. An intense band observed at \sim 360–385 nm could be due to ligand-to-metal charge-transfer (LMCT: PhO $\rightarrow V_{(d\pi)}$] transition and the remaining bands appearing in the UV-region are assignable to the intraligand transitions [37]. The band due to $\pi \rightarrow \pi^*$ transitions

tion moves to lower energy at (\cong 400 nm). Spectra of VO(IV) with various ligand arising from the tetragonal compression caused by V=O bonds, which results in further splitting of d orbitals and give rise to ${}^{2}B_{2} \rightarrow {}^{2}E (d_{xy} \rightarrow d_{xz}, d_{yz}), {}^{2}B_{2} \rightarrow {}^{2}B_{1} (d_{xy} \rightarrow d_{x2-y2}), {}^{2}B_{2} \rightarrow {}^{2}A_{1}(d_{xy} \rightarrow d_{z2})$ These values are consistent with distorted octahedral structure for oxovanadium(IV) [38].

3.7. ESR spectra

All spectra of all the oxovanadium(IV) polymer complexes (1–4) were recorded. In polycrystalline state at room temperature and in DMF solution at 77 K, the compound (1) is axial with g_{\parallel} = 1.982

	1	2	3	4
$g_{\rm ll}$	1.952	1.955	1.950	1.951
g_{\perp}	1.985	1.984	1.985	1.980
$A_{\rm ll}$	159.60×10^{-4}	141.51×10^{-4}	159.67×10^{-4}	162.68×10^{-4}
A_{\perp}	51.66×10^{-4}	50.86×10^{-4}	51.32×10^{-4}	52.41×10^{-4}
α^2	0.916	0.818	0.712	0.938
B^2	0.938	0.870	0.937	0.962

^a See Table 1.

and g_{\perp} = 2.069 and the other compounds are isotropic with ~1.985. All the compounds in DMF solution (Table 3) show well-resolved axial anisotropy with $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\rm I}$ relationship characteristic of an axially compressed $d_{\rm xy}$ configuration [39]. The absence of any ligand hyperfine lines in the g_{\parallel} features due to nitrogen indicates that the unpaired electron, for most of the times staying in the b_{2g} ($d_{\rm xy}$, ²B₂ ground state) orbital localized on metal, thus excluding the possibility of its direct interaction with the ligand [40,41].

The ESR parameters $g_{||}, g_{\perp}, A_{||}$ and A_{\perp} and energies of d-d transitions were used to evaluate the molecular orbital coefficients α^2 and β^2 for the polymer complexes by using the following equations:

$$\alpha^{2} = (2.00277 - g_{\parallel})E_{d-d}/8\lambda\beta^{2}$$
$$\beta^{2} = \frac{7}{6}\left[\left(-\frac{A_{\parallel}}{P}\right) + \left(\frac{A_{\perp}}{P}\right) + \left(g_{ll} - \left(\frac{5}{14}\right)g_{\perp}\right)\right) - \left(\frac{9}{14}\right)g_{e}\right]$$

where $P = 128 \times 10^{-4}$ cm⁻¹, $\lambda = 135$ cm⁻¹ and *E* is the energy of d-d transition. The lower values for α^2 compared to β^2 indicate that in-plane σ bonding is more covalent than in-plane π bonding [42]. The in-plane π bonding parameter β^2 observed are consistent with those observed for McGarvey and Kilvelson for vanadyl complexes of acetylaceton. The ESR data reveals that Bipy. > Py >en (slightly) increase in $A_{\rm II}$ while en < Bipy. < Py in $g_{\rm II}$.

3.8. Thermal analysis

The thermal decomposition process of polymeric complexes involves three decomposition steps. The polymer complexes show no mass loss up to 180 and 280 °C, revealing the absence of either water or solvent molecules in these polymeric complexes. The first decomposition step takes place in the temperature range ~175-265 and ~275-485 °C with endothermic DTA peaks at ~225, ~325, ~430, and ~450 °C, respectively, corresponding to the decomposition of half of the molecule. The second step occurs in the 260-595 and 485-655 °C range corresponding to the decomposition of remaining half of the molecule. The DTA curve gives peaks at ~310 (exo), and weak endothermic multiple in the ~440-655 °C range for polymeric complexes. The third step take place in the 595-1080°C range corresponding to the decomposition of ethylenediamine, bipyridine and pyridine molecule, respectively leaving anhydrous metal oxide as residue.

4. Concluding remarks

From the overall studies presented, it is concluded that in the vanadium(IV) polymer complexes.

H₂L was characterized by analytical and spectral methods before using it for the preparation of complexes.

 H_2L behaves as a chelating tridentate dibasic ligand, bonding through oxygen of enolic/phenolic group and azody group nitrogen atom forming a six/five membered ring as shown in Fig. 4. The CS breathing mode of the ligand is remains unaltered in the polymer

complexes commensurate with absence of coordinations through the sulphur atom of the CS group [24].

Based on various studies like elemental analyses, conductance measurements, magnetic susceptibilities, infrared, UV–vis and ESR spectral studies a octahedral geometry as a shown in Figs. 2 and 3, may be proposed for all the polymeric complexes.

 $\{[(VO)L]_2\}_n$ (1) and $[(VO)L.B]_n$ (2–4), L is the doubly deprotonated allylazorhodanine ligand and B is the bidentate heterocyclic base *viz.*, bipy, Py and aliphatic en as shown in Figs. 2 and 3.

We report here on some unknown chemistry of oxovanadium(IV) polymeric complexes showing ESR activity. Three ternary oxovanadium(IV) complexes having ONO-donor ligand and bases are synthesized and structurally characterized.

A high affinity of chelation of the ligand towards VO(IV) ions was noticed according to the increasing charge density of the metal ion towards the increasing of their coordination affinities.

The results arising from the present investigations confirm that the selected 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5- $[(o.hydroxyl phenyl)](H_2L)$ ligands are suitable for building a supramolecular structure. Moreover, since the azo polymer compounds experience photochemical isomerization and are therefore of interest for applicative purposes, polymer complexes containing the 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5- $[(o.hydroxyl phenyl)](H_2L)$ moiety combine features which could be useful in molecular materials.

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