

SYNTHESES AND SPECTRAL ASPECTS OF OXIDOVANADIUM(IV) CHELATES DERIVED FROM ONS DONOR THIOSEMICARBAZONES

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3.1. Introduction

Vanadium is a hard, silvery gray, ductile and malleable transition metal. It has good corrosion resistance to alkalis, sulfuric acid, hydrochloric acid and salt waters. Vanadium resists corrosion due to a protective film of oxide on the surface. Common oxidation states of vanadium include +2, +3, +4 and +5. Andrés Manuel del Río discovered vanadium in 1801 by analyzing a new lead-bearing mineral called "brown lead" and named the new element *erythronium* (Greek for "red") since, upon heating, most of its salts turned from their initial color to red. The element was rediscovered in 1831 by Nils Gabriel Sefström, who named it vanadium after the German goddess of beauty and fertility, Vanadís.

Vanadium occurs naturally in about 65 different minerals among which are patronite, vanadinite, carnotite and bauxite and in fossil fuel deposits. The metal oxidizes readily above 660 °C to form vanadium pentoxide (V_2O_5), the most important industrial vanadium compound, which is used as a catalyst for the production of sulfuric acid and maleic

anhydride and in making ceramics. It is added to glass to produce green or blue tint.

In biology, vanadium is an essential component of some enzymes, particularly the vanadium nitrogenase used by some nitrogen-fixing microorganisms. It is used by some life forms as an active center of enzymes, such as the vanadium bromoperoxidase of some ocean algae. Vanadium is probably a micronutrient in mammals, including humans, but its precise role in this regard is unknown.

Since the recent discovery of the presence of trivalent vanadium in several biological systems, the interest for vanadium(III) chemistry has considerably grown [1]. The trivalent state is indeed one of its unstable oxidation states and can be easily oxidized to vanadium(IV) or vanadium(V) especially in solution where these reactions can be very fast. The chemistry of oxidovanadium(IV) has received considerable attention as the VO^{2+} unit can readily bond to four and five donor atoms to form VO_4 and VO_5 complexes respectively. Additional interest has been generated in the coordination chemistry of oxidovanadium(IV), oxidovanadium(V) and dioxidovanadium(V) complexes, as they model vanadium containing enzymes and serve as good oxidation catalysts. Oxidovanadium(IV) complexes find use in chemical reactivity studies either as models for V-O bond reactivity [2] or as potential free radicals.

Among the biological activities of vanadium, an interesting mimetic antidiabetic effect is the most striking, the effect being provided by the oxidation states of vanadic(III), vanadyl(IV) and vanadate(V) [3]. Medicinal applications of vanadium compounds have focussed on their *in vitro* and *in vivo* activity in the treatment of insulin deficiency, type I

diabetes and insulin tolerance, type II diabetes which is by far the more common form frequently found with elderly people and increasingly also a problem for obese young people [4]. In addition to the therapeutic effect of vanadium ion and vanadium complexes, they have a preventive effect also [3]. Dioxidovanadium(V), oxidovanadium(IV) or vanadium(III) complexes [5-9] with thiosemicarbazones are interesting because of their significant pharmacological activities and catalytic roles in many biological systems and industrial processes [10-13]. Having all these facts in mind, it was thought worthwhile to study the coordination chemistry of oxidovanadium(IV) complexes derived from 5-bromo-3-methoxysalicylaldehyde-N(4)-phenyl thiosemicarbazone (H_2L^1).

3.2. Experimental

3.2.1. Materials

Vanadyl sulfate monohydrate (Sigma-Aldrich), 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) were of Analar grade and were used as received. Solvents used were methanol and DMF.

3.2.2. Synthesis of the thiosemicarbazone

The synthesis of thiosemicarbazone H_2L^1 is already discussed in Chapter 2.

3.2.3. Syntheses of the complexes

3.2.3.1. $[VOL^1phen]$ (1)

Aqueous solution of vanadyl sulfate monohydrate (0.081 g, 0.5 mmol) was added to a stirred mixture of H_2L^1 (0.190 g, 0.5 mmol) in DMF and

methanol (1:1 v/v) and 1,10-phenanthroline (0.099 g, 0.5 mmol) in methanol. The resultant solution was refluxed for three hours. The brown product obtained was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 51.45 (51.85); H, 2.67 (3.22); N, 11.07 (11.20); S, 5.11 (5.13). Yield: 77%

3.2.3.2. [VOL¹bipy] (2)

To a stirred mixture of H₂L¹ (0.190 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 2,2'-bipyridine (0.078 g, 0.5 mmol) in methanol, aqueous solution of vanadyl sulphate monohydrate (0.081 g, 0.5 mmol) was added. The resultant solution was refluxed for 3 hours and the brown product separated out was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 49.41 (49.93); H, 3.66 (3.35); N, 11.18 (11.65); S, 5.77 (5.33). Yield: 72%

3.3. Results and discussion

Two oxidovanadium complexes of the thiosemicarbazone were synthesized. They were synthesized by refluxing metal salt, corresponding heterocyclic bases and thiosemicarbazone in 1:1:1 ratio. Both of the complexes are brown in colour and are soluble in solvents like DMF and DMSO. In both the complexes, the thiosemicarbazone exists in the thioiminolate form and act as dideprotonated tridentate ligands coordinating through phenolic oxygen, thioiminolate sulfur and azomethine nitrogen. Both of the complexes are monomeric mixed ligand metal chelates. They are characterized by the following physico-chemical methods.

3.3.1. Elemental analyses

The analytical data indicate that the complexes are analytically pure. The elemental analyses data are consistent with the general formula [VOL¹B], where L¹ is the doubly deprotonated thiosemicarbazone ligand and B is the bidentate heterocyclic bases *viz.* phen, bipy. However we could not isolate single crystals of suitable quality for XRD studies for any of these complexes.

3.3.2. Molar conductivity and magnetic susceptibility measurements

The conductivity measurements were made in DMF (10⁻³ M) and all the complexes were found to be non-electrolytes [14]. The room temperature magnetic moments of the complexes **1** and **2** in the polycrystalline state are 1.51 and 1.62 B.M. respectively, which are very close to the spin-only value for a *d*¹ system (1.73 B.M.) [15]. Both the complexes are EPR active due to this unpaired electron.

Table 3.1. Molar conductivity and magnetic moments of V(IV) complexes

Compound	λ_m^a	μ_{eff} (B.M.)
[VOL ¹ phen] (1)	18.6	1.51
[VOL ¹ bipy] (2)	29.0	1.62

^a = mho cm² mol⁻¹

3.3.3. Infrared spectra

A comparison of the IR spectra of H₂L¹ and the metal complexes shows that significant variations have occurred in the characteristic frequencies upon complexation. The tentative IR spectral assignments of

the complexes are listed in Table 3.2. In all the complexes, the bands due to O-H and $^2\text{N-H}$ stretching vibrations are absent which is a clear evidence for the coordination of the thiosemicarbazone in the dideprotonated form. The band corresponding to azomethine bond, $\nu(\text{C=N})$, shifts to higher energy on coordination due to the combination of $\nu(\text{C=N})$ with the newly formed C=N bond which results from the loss of the thioamide hydrogen from the thiosemicarbazone moiety [16-20]. The band at 1333 cm^{-1} present in H_2L^1 shifts to lower wavenumbers in both the complexes and this can be assigned to the $\nu(\text{C-S})$ vibration suggesting the change of bond order and strong electron-delocalization upon chelation. This shows that the H-N-C=S in the ligand has transformed to N=C-S-H thereby coordinating to vanadium in the thioiminolate form. Coordination *via* thioiminolate sulfur is also indicated by the negative shift of the band assigned to $\delta(\text{C=S})$ vibration in the thiosemicarbazone [21]. The bands in the range $439\text{-}455\text{ cm}^{-1}$ indicates the coordination of azomethine nitrogen to vanadium centre. The increase in frequency of $\nu(\text{N-N})$ bands in complexes, due to the increase in double bond character is another proof for the coordination of the thiosemicarbazone through the azomethine nitrogen [22]. The broad absorption band at 3441 cm^{-1} assigned to phenolic -OH of H_2L^1 has disappeared in the complexes which indicate the coordination of the phenolic oxygen to the vanadium atom. The IR spectra of these complexes display bands characteristic of coordinated heterocyclic bases [23]. Further, the intense bands observed at 964 cm^{-1} for complex **1** and 954 cm^{-1} for complex **2** correspond to the terminal V=O stretching band [24]. Figs. 3.1 and 3.2 depict the infrared spectra of these complexes.

In both the complexes, the thiosemicarbazone H_2L^1 acts as a dianionic tridentate ligand coordinating to vanadium through O, N and S atoms and the two nitrogen atoms of heterocyclic bases occupy the fourth and fifth coordination positions of vanadium.

Table 3.2. IR spectral assignments (cm^{-1}) of thiosemicarbazone and its oxidovanadium(IV) complexes

Compound	$\nu(O-H)$	$\nu(C=N)$	$\nu(C=N)^a$	$\nu(N-N)$	$\nu(C=S)/\nu(C-S),$ $\delta(C=S)/\delta(C-S)$	$\nu(C-O)$	$\nu(V-O)$	$\nu(V-N)$
H_2L^1	3441	1540	----	1071	1333, 857	1267	----	----
[VOL ¹ phen] (1)	----	1588	1539	1100	1295, 845	1237	502	455
[VOL ¹ bipy] (2)	----	1588	1544	1110	1306, 846	1228	474	439

^a = newly formed C=N bond

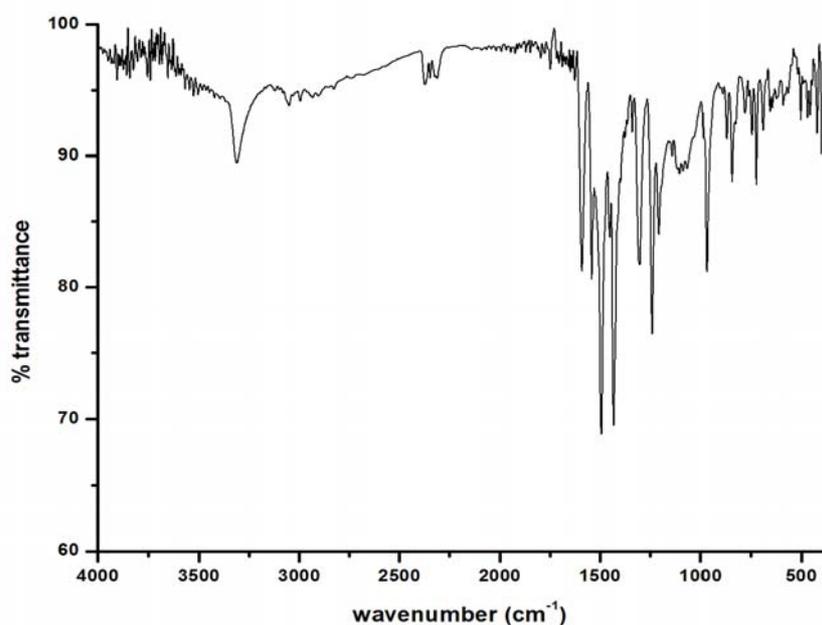


Fig. 3.1. Infrared spectrum of [VOL¹phen] (1).

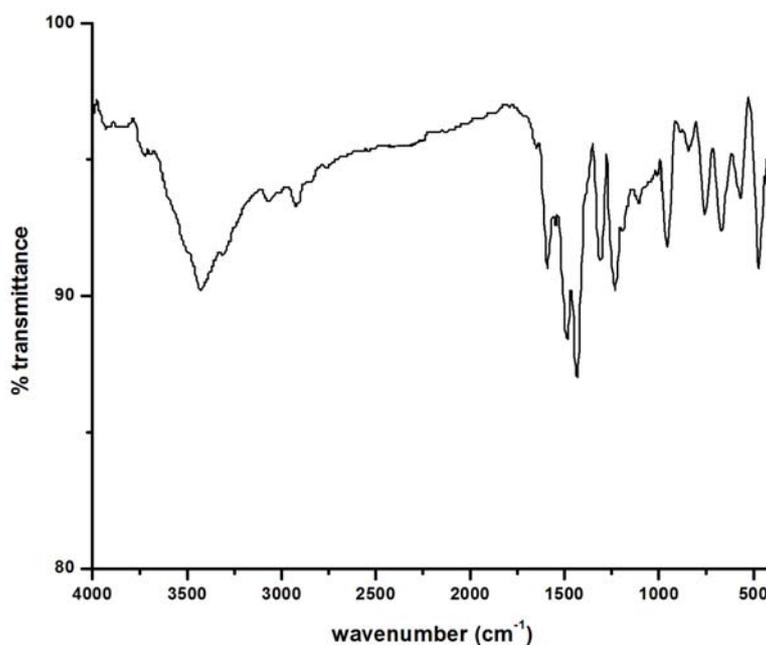


Fig. 3.2. Infrared spectrum of [VOL¹bipy] (2).

3.3.4. Electronic spectra

The electronic spectra of both the complexes were taken in DMF. The significant electronic absorption bands in the spectra of H₂L¹ and the oxidovanadium complexes are given in Table 3.3. The electronic transitions found in the free ligand due to imine function of thiosemicarbazone moiety were slightly shifted on complexation. The shift of the bands due to intraligand transitions is the result of the weakening of the C=S bond and the extension of conjugation upon complexation [25]. The shift occurs also due to coordination *via* phenolic oxygen and azomethine nitrogen [26] and is an indication of the enolization followed by the deprotonation of the thiosemicarbazone during complexation. The intraligand n→π* and π→π* transitions are assigned to bands in the range 28280-30200 cm⁻¹ for these complexes. In all the complexes, intense bands

in the 24810-26790 cm⁻¹ range are assigned to ligand to metal charge transfer transitions arising from the phenolate oxygen to an empty *d* orbital of the vanadium(IV) center [5]. Fig. 3.3 represents the electronic spectra of the complexes.

Ballhausen and Gray (BG scheme) have provided a convenient energy level scheme for VO(IV) type complexes [27]. In general, three absorptions are observed in the spectra of most of the oxidovanadium complexes, arising from the tetragonal compression caused by V=O bond, which results in further splitting of *d* orbitals and gives rise to three spin allowed transitions, ²E ← ²B₂ (ν₁) (*d*_{xy} → *d*_{xz}, *d*_{yz}), ²B₁ ← ²B₂ (ν₂) (*d*_{xy} → *d*_{x²-y²}), ²A₁ ← ²B₂ (ν₃) (*d*_{xy} → *d*_{z²}) [28]. Since the ²E and ²B₁ levels are very close in energy, they may cross and result in a weak broad band. In complex **1**, the expected *d-d* bands are not observed and are probably obscured by the intense LMCT absorptions. We could locate only one band in [VOL¹bipy] (**2**) due to the masking by high intensity charge transfer bands (Fig. 3.4).

Table 3.3. Electronic spectral assignments (cm⁻¹) of thiosemicarbazone and its V(IV) complexes

Compound	n→π*/π→π*	LMCT	d-d
H ₂ L ¹	28770, 30490
VOL ¹ phen (1)	28380, 30200	24810
VOL ¹ bipy (2)	28280, 30140	24790	14160

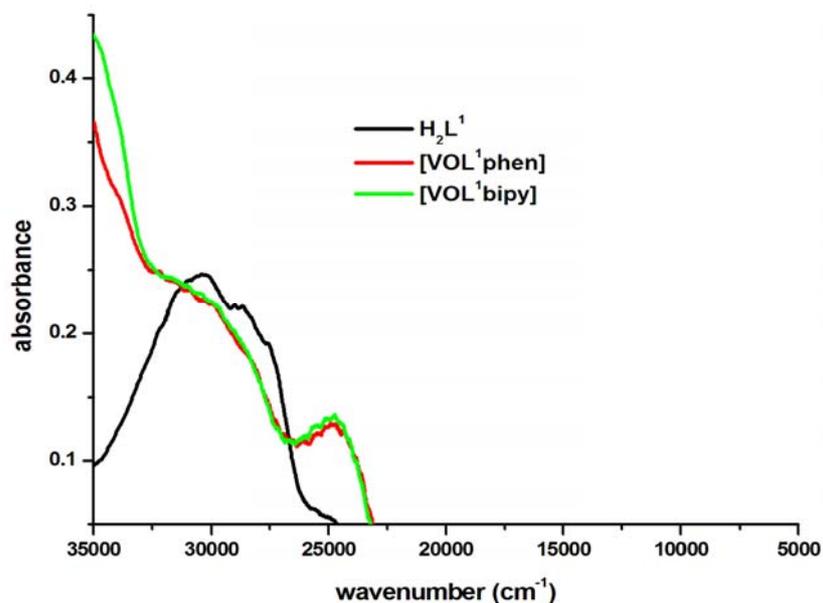


Fig. 3.3. Electronic spectra of H_2L^1 and its oxidovanadium complexes.

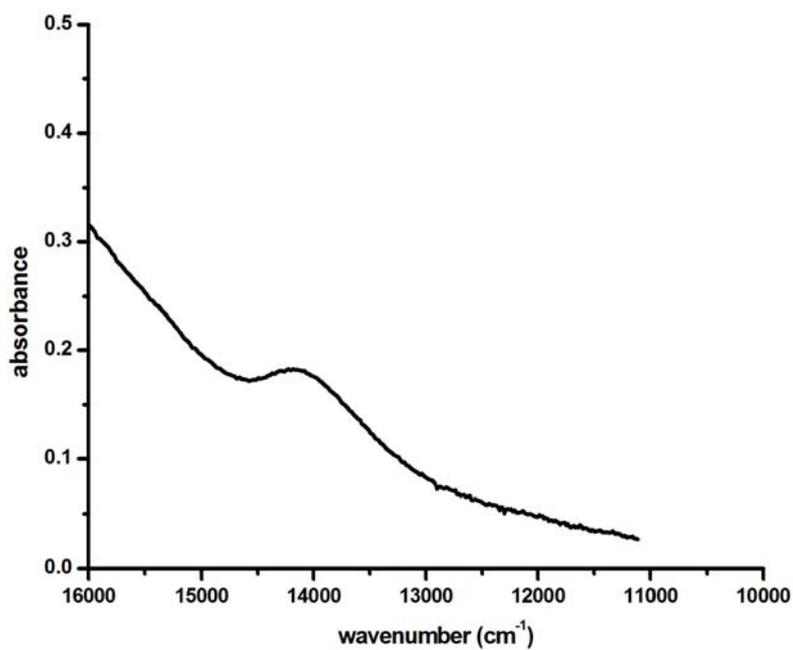


Fig. 3.4. Visible spectrum of $[VOL^1bipy]$ (2).

3.3.5. EPR spectra

In Electron Paramagnetic Resonance spectroscopy, radiation of microwave frequency is absorbed by a molecule or ion having unpaired electron(s). Thus it is a convenient way to probe the electronic structure of paramagnetic compounds.

In vanadyl complexes, vanadium is in +4 oxidation state with d^1 configuration and since the orbital angular momentum is quenched by the crystalline fields, the paramagnetism of the vanadyl ion arises from the single unpaired electron. In V(IV) complexes value of g is below the value for free electron. The spin of ^{51}V nucleus is $I = 7/2$. In mononuclear V(IV) complexes, the EPR signals are split into eight and in binuclear complexes, fifteen hyperfine lines. Under the influence of magnetic field, the electronic ground state ($S = 1/2$) is split into two ($m_s = +1/2$ and $-1/2$) and additional splitting occurs through the different magnetic orientations of the nuclear spin (m_I).

VO^{2+} is one of the most stable diatomic cation and its paramagnetism is almost due to spin angular momentum and EPR absorptions are obtained over a wide range of temperature including room temperature [29].

EPR spectra of all the oxidovanadium(IV) complexes were recorded in polycrystalline state at 298 K and in DMF at 77 K and the spectral parameters are summarized in Table 3.4. The EPR spectrum of complex **1** in DMF at 77 K is simulated and the experimental (red) and simulated (blue) best fit is included. Simulation was performed using Matlab 7.8.0 (R2009a) software and the EasySpin 4.0.0 package [30]. Figs. 3.5-3.8 depict the EPR spectra of the oxidovanadium complexes.

The EPR spectra of complexes **1** and **2** in the solid state at 298 K are isotropic in nature and hence only one g value, arising due to dipolar interactions and enhanced spin-lattice relaxation. In DMF at 77 K, both the complexes displayed well resolved axial anisotropy with two sets of eight line pattern which result from coupling of the electron spin with the spin of the ^{51}V nucleus ($I = 7/2$). They are found to exhibit $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationship, characteristic of an axially compressed d_{xy}^1 configuration [31].

The absence of any superhyperfine lines in the spectrum is an explicit indication of the sole electron lying in the d_{xy} orbital (2B_2 ground state), localized on metal, thus excluding the possibility of its direct interaction with the azomethine nitrogen of the thiosemicarbazone [32,33].

The anisotropic parameters are related with isotropic parameters by the equations, $A_{\text{iso}} = 1/3(A_{\parallel} + 2A_{\perp})$ and $g_{\text{iso}} = 1/3(g_{\parallel} + 2g_{\perp})$ [34]. In both compounds, the g_{iso} values calculated are near to the value obtained from the polycrystalline spectra which suggests that the molecules retain their structural identity in solution.

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

$$\alpha^2 = \frac{(2.00277 - g_{\parallel})E_{d-d}}{8\lambda\beta^2}$$

$$\beta^2 = \frac{7}{6} \left[\left(\frac{-A_{\parallel}}{P} \right) + \left(\frac{A_{\perp}}{P} \right) + \left(g_{\parallel} - \frac{5}{14}g_{\perp} \right) - \frac{9}{14}g_e \right]$$

where $P = 128 \times 10^4 \text{ cm}^{-1}$, $\lambda = 135 \text{ cm}^{-1}$ and E_{d-d} is the energy of $d-d$ transition.

Table 3.4. EPR spectral parameters of oxidovanadium(IV) complexes in the polycrystalline state at 298 K and in DMF at 77 K.

Compound	Polycrystalline state at 298 K		DMF (77 K)						
	g_{iso}	$g_{ }$	g_{\perp}	g_{av}	$A_{ }^a$	A_{\perp}^a	A_{av}^a	α^2	β^2
[VOL ¹ phen] (1)	1.983	1.955	1.970	1.965	175	54	95	---	0.979
[VOL ¹ bipy] (2)	1.985	1.955	1.980	1.972	176	61	98	0.668	0.938

^aExpressed in units of cm^{-1} multiplied by a factor of 10^{-4} .

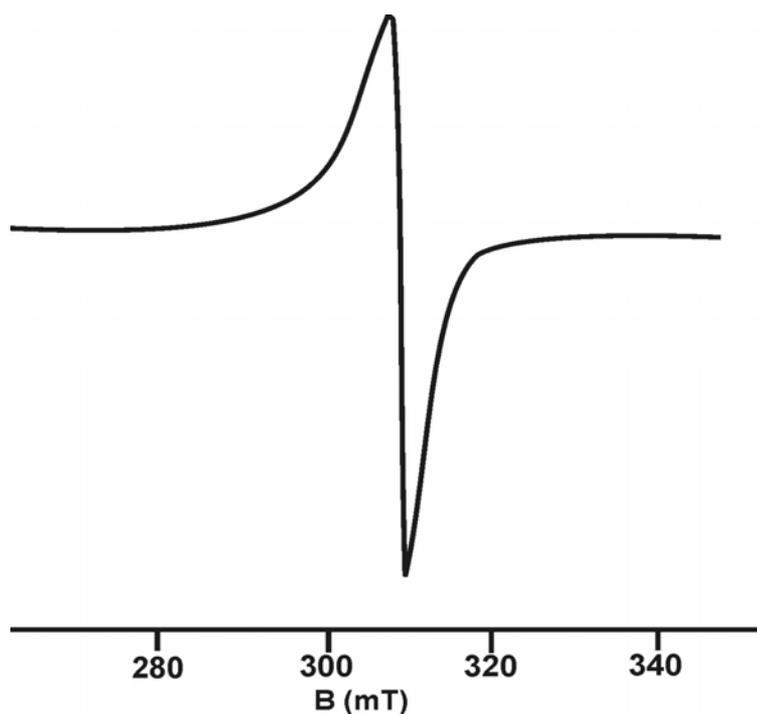


Fig. 3.5. EPR spectrum of [VOL¹phen] (1) in polycrystalline state at 298 K.

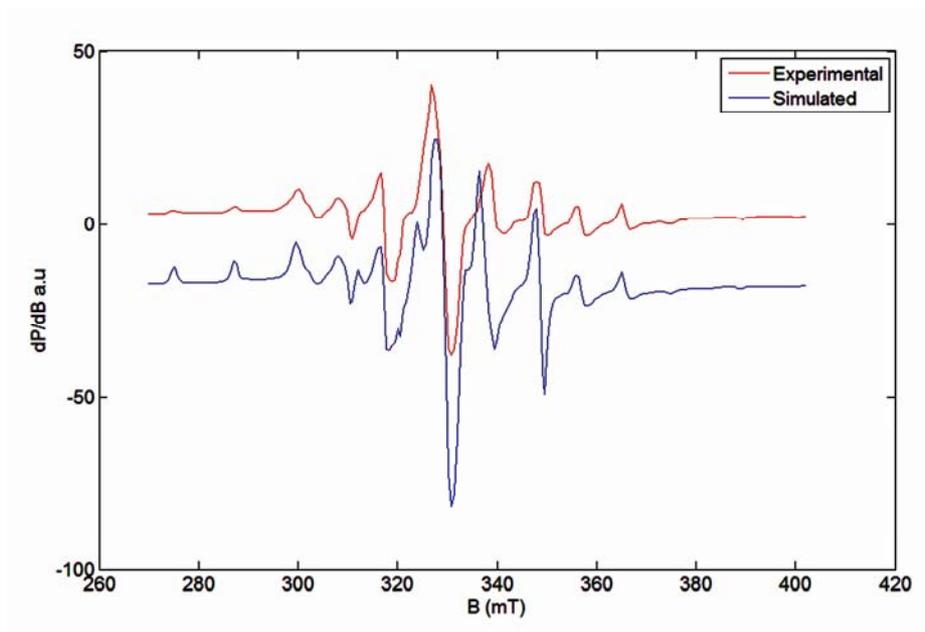


Fig. 3.6. EPR spectrum of [VOL¹phen] (1) in DMF at 77 K.

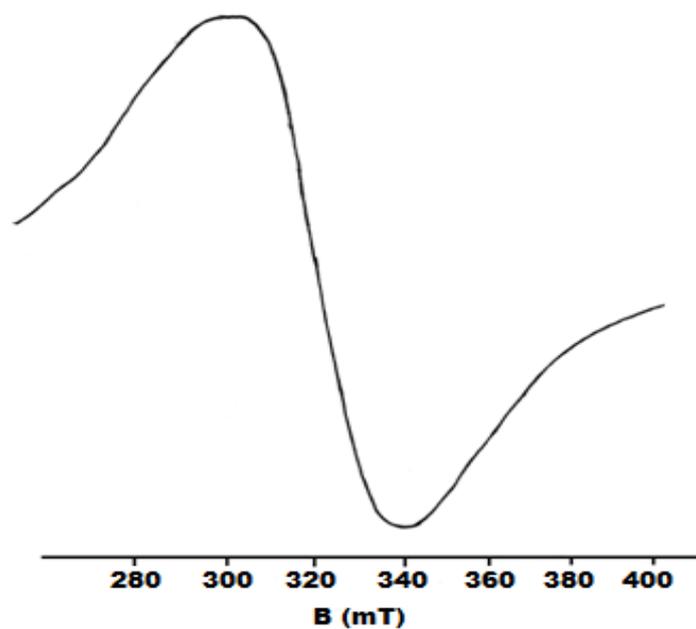


Fig. 3.7. EPR spectrum of [VOL¹bipy] (2) in polycrystalline state at 298 K.

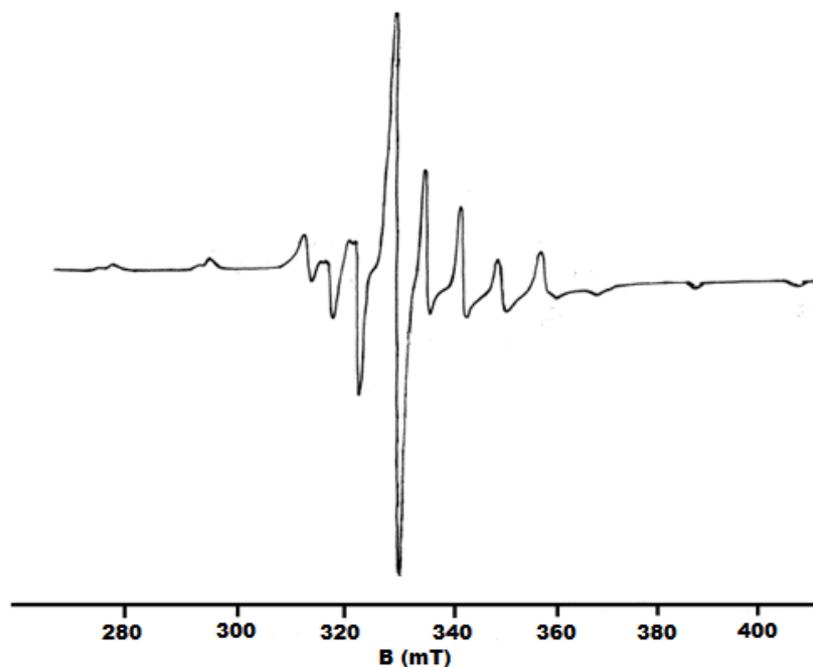


Fig. 3.8. EPR spectrum of [VOL¹bipy] (2) in DMF at 77 K.

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