



SYNTHESIS AND SPECTROSCOPIC STUDIES ON OXOVANADIUM COMPLEX WITH LIGANDS HAVING N, N-DONOR SITES

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ABSTRACT

The present investigation is concerned with a method by the reaction of vanadylsulphate with nitrogen containing ligands N, N donor sites like dicyandiamide, methyldicyandiamide and phenyldicyandiamide in methanol and refluxed. The tentative structure of these complexes has been proposed on the basis of elemental analysis, magnetic moment and spectral (IR, EPR) data. The IR and EPR spectra of all the complexes were recorded at room temperature and at liquid nitrogen temperature. The room temperature EPR spectrum shows anisotropy because the band is observed separately.

Keywords: Vanadium (IV) complexes compound, Elemental analysis, IR, EPR spectral data and magnetic moment data.

1. INTRODUCTION

Among the transition metals, the chemistry of vanadium has received considerable attention due to the significant role in a variety of chemical and biological systems [1, 2]. The coordination chemistry and the reactivity of vanadium have continued to play a significant role not only because of the physiological relevance of this transition metal but also for its activity in various industrial processes.

Vanadium compounds can be in a variety of oxidation states (-1 to 5), vanadium (IV) is of considerable interest since it is the most stable compound with the metal in a d^1 configuration. This paramagnetic species can be studied using EPR spectroscopy. The V^{4+} ion usually forms oxo- compound VO^{2+} . M.M. Jones [3] reported the preparation and properties of a number of complexes between the vanadyl ion and diketones having five coordinated vanadium (IV). U. casellato and P.A. Vigato [4] discussed the involvement of metal chelation in many important biological processes where the coordination can occur between a variety of metal ions and a wide range of ligands. Particular attention have been given in the synthesis of oxo vanadium complexes of the ligand R sal N $(CH_2)_n OH$ (R=H, 5-Cl, 5-Br, 5- NO_2 , 5-MeO, 3- NO_2 , 3MeO; n= 2, 3). The room temperature magnetic moments of the complexes with the ligands R Sal N $(CH_2)_n OH$ are lower (0.89-1.41 BM) than the complexes with R Sal N $(CH_2)_n OH$. It was inferred on

the basis of the magnetic data that the alcoholic oxygen are bridging rather than the phenolic oxygen. The prediction of the structure was made on the basis of the magnetic data. The magnetic moment of these complexes decreased considerably on the temperature was lowered in accordance with an antiferromagnetic exchange interaction in binuclear structure. S.K Sengupta et. al. [5] synthesized three oxovanadium (IV) complexes with 14-membered macro cyclic ligands derived from dithioxomides and reported the square pyramidal geometry for the oxovanadium (IV) complexes based on the spectral data. Extensive spectroscopic research works have been published [6-8]. As a part of the investigations we have synthesizes there oxo vanadium (IV) complexes of substituted dicyandiamide with a limited view to find out magnetic exchange interaction in the complexes prepared. Research interest in oxidovanadium chemistry derives from its ability in several biological and industrial processes like antimicrobial, spermicidal, antioxidant, antitumor, DNA binding [9] and recently as insulin mimetic [10]. The vital role of vanadium in different chemical and biological system has motivated the development of vanadium chemistry. The coordination chemistry of nitrogen and oxygen donor ligand is an active area of research. Biologically, vanadium is known for its exceptional ability to interact with biomolecule in both cationic and anionic forms and its numerous oxidation states. Several therapeutic effects have been

described for vanadium including hormonal, cardiovascular and anti-carcinogenic [11-13] vanadium complexes have potential application in catalysis [14] biological modeling [15] and design of molecular magnets [16]. It is also well known that vanadium complexes have the potential to take part in nitrogen fixation [17] and halo peroxidation [18] as insulin mimetic [19] antitumor [20] and an amoebic agent [21]. Bis (acetyl-acetonato) oxo vanadium (IV) [VO(acac)₂] is also used as a new class of cancer specific MRI contrast agents that are nontoxic and highly sensitive to cancer metabolism.

In the development of new anticancer drugs considerable efforts have been focused on vanadium metal complexes particularly biocompatible copper (II) complexes that can bind and cleave DNA under physiological condition [22]. Vanadium metal complexes containing ligand systems having versatile hydrogen bonding potential have been used to bind DNA bases and other anions and to construct network of coordinated complexes connected through intermolecular interaction [23] DNA binding metal complexes can also be used in the development of anti-inflammatory, antifungal, antibacterial or anticancer reagent [24]. Compounds containing DNA bases are of considerable interest owing to their hydrogen bond mediated interactions and their wide range of biological activities [25] several workers have reported the potent antitumor, antiviral and antifungal activities of some marine natural products guanidine groups and their artificial analogs [26]. Only few studies have been reported for the interaction of vanadium complexes with DNA and generally, they have been restricted to case when vanadium is in its highest oxidation state [27-29]. On the other hand dicyandiamide is being employed in a wide variety of applications and utilized as an intermediate for a number of resins and organic nitrogen compound biguanides and guanides. Recently, binuclear copper (II) complexes of dicyandiamide [30,31] and phenyl dicyandiamide [32,33] prepared in different alcohols have been reported and some of the complexes are reported to exhibit fungicidal and bactericidal activities [34,35]. Thus, considering the importance of vanadium complexes and dicyandiamide as well as its DNA interaction we report here a new oxovanadium (IV) complexes [VO(acac)₂DCDA] H₂O using acetylacetonate (acac) and dicyandiamide (DCDA) as ligands. The synthesized complexes have been characterized by chemical analysis, IR, UV, ESR, TGA- TDA luminescence, cyclic voltammetry and powdered XRD analysis. The interaction of these

complexes with CT- DNA (calf thymus DNA) was investigated using UV- vis absorption titration, cyclic-voltammeter and thermal denaturation.

2. MATERIAL AND METHODS

All the chemicals were of reagent grade. Methylamine hydrochloride, Sodium dicyanide, Butanol, Aniline, Hydrochloric acid, Sodium nitrite and Dicyandiamide were directly purchased from market farm. All the solvents were of analytical grade.

The prepared complexes were characterized for the elemental analysis (carbon, hydrogen and nitrogen) at the CDRI, Lucknow, magnetic susceptibility at IACS, Kolkata, EPR at BARC Mumbai (Trombay), IR spectra at RSIC, Guwahati.

2.1. General procedure for the synthesis of Ligands

2.1.1. Methyl dicyandiamide

Methylamine hydrochloride (6.8g), sodium dicyanimide (8.9g) and butanol 50ml were refluxed for 3 hours. The cooled suspension was filtered and filtrate was evaporated. The compound was dried for 48 hours over NaOH and paraffin wax in a vacuum.

The yield was 92% and Melting point was 209°C. Elemental analysis for Anal (%) N59, C33.5, H7.0, IR data of the substituted dicyandiamide (cm⁻¹) 334.0s, 1610sbr, 900w. (br = broad; m = medium; s = strong; w = weak; vs = very strong; wbr = weak broad; sbr = strong broad).

2.1.2. Phenyl dicyandiamide

Aniline (23g) was diazotized at 0-5°C 2.5N hydrochloric acid (250cc) with sodium nitrite (17.5g) in 100cc of water and added to dicyandiamide (23g) in water (700cc) at 20°C. Excess of 10N NaOH was added to maintain a strong alkaline reaction and refluxed for half an hour. The golden-yellow solution was acidified with acetic acid. The precipitate was filtered off.

The yield and melting point were 90% and 195-196°C respectively. The elemental analysis for Anal (%) N34.9, C59.0, H4.9, and IR data of the substituted dicyandiamide (cm⁻¹) 3230m, 1565m, 1301m, 719wbr, 3125w, 1493m, 1205m, 690 w, 2167 vs, 1449 m, 908 m, 1656 m, 1396 w, 746 m.

2.2. General procedure for the synthesis of vanadyl (IV) complexes

2.2.1. Synthesis of [VO(AMUH)SO₄]

Vanadylsulphate monohydrate (7.0g) and dicyandiamide

(7.4g) were dissolved in methanol (50ml). The mixture was refluxed on a water bath for 16 hours. Light blue colour changed to yellowish brown solution and kept in a refrigerator. The crystal (complexes) separated out and recrystallized from acetone and dried in air.

The yield was 70%, colour- light yellow, m. p. 170°C, magnetic moment μ_{eff} (1.8551BM) Elemental analysis for Anal (%) C12.14, H2.70, N18.90, V17, 18, IR data (cm^{-1}) $\nu(\text{C}=\text{N}$, 1734s), 1696s, 160m and $\nu(\text{SO}_4^{2-})$, 1081s, 948vw ($\nu = (\text{nu})$ wave number)

2.2.2. Synthesis of [VO(MAMUH)SO₄]

Vanadylsulphate monohydrate (0.722g) and methyl dicyandiamide (0.856g) were dissolved in methanol (50ml). The mixture was refluxed on a water bath for 16.40 hours. The light blue colour changed to brown solution and kept in the refrigerator. The crystal (complexes) separated out and recrystallized from acetone and dried in air.

The yield was 60%, colour-light brown, m.p. 162°C, magnetic moment μ_{eff} (1.4BM), elemental analysis for Anal (%) C16.50, H3.42, N19.18, V17.49, IR data (cm^{-1}) $\nu(\text{C}=\text{N}$, 1754s) 1689s, 1624s and $\nu(\text{SO}_4^{2-})$, 1100w 955s.

2.2.3. Synthesis of [VO(phAMUH)SO₄].3H₂O

Vaandylsulphate monohydrate (1.5123g) and phenyl dicyandiamide (2.6737g) were dissolved in methanol (about 50ml). The mixture was refluxed on a water bath for 25.50 hours. The colour of light blue changed to

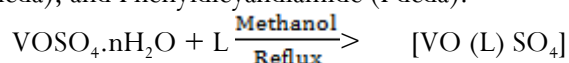
yellowish brown solution and kept in the refrigerator. The crystal (complex) separated out and recrystallized from acetone and dried in air.

The yield was 55% and the melting point was 184°C, magnetic moment μ_{eff} (1.0BM), and elemental analysis for Anal (%) C25.04, H3.00, N13.26, V12.50, IR data (cm^{-1}) $\nu(\text{C}=\text{N}$, 1724s) 1672s, 1584s and $\nu(\text{SO}_4^{2-})$, 118m 964s.

3. RESULTS AND DISCUSSION

The ligands (L) react with Oxovanadium (IV) sulphate in methanol and products of type [VO (L)] SO₄] have been isolated.

Where L = Dicyandiamide (Dcda), Methyl dicyandiamide (Mdcda), and Phenyl dicyandiamide (Pdcda).



The elemental analyses of the complexes oxovanadium (IV) are given in the Table (1). The procedure and used for the preparation and isolation of these compounds gave materials of good purity as supported by their analysis. The complexes are brown in colour insoluble in organic solvents. So, our study was confirmed only on the solid state.

3.1. Estimation of Nitrogen, Carbon and Hydrogen

Elemental analysis of nitrogen, carbon and hydrogen were carried out at Central Drug Research Institute (CDRI) Lucknow and found as Elemental analytical data of oxovanadium (IV) complex.

Table 1: Elemental analysis of the complexes compound

Compounds and colour	Found (calculated) (%)			
	C	H	N	V
1.VO(AMUH)SO ₄ Light Yellowish brown	12.14(12.12)	2.70(2.69)	18.90(18.85)	17.18(17.17)
2.VO(MAMUH)SO ₄ Light Brown	16.50(16.38)	3.42(3.41)	19.18(19.11)	17.49(17.40)
3.VO(PhAMUH)SO ₄ .3H ₂ O Yellowish brown	25.04(26.40)	3.00(2.93)	13.26(13.69)	12.50(12.46)

The characteristic IR spectral bands of oxovanadium (IV) complexes are discussed as, for pure phenyl dicyandiamide show as strong $\nu(\text{C} \equiv \text{N})$ band at 2167 cm^{-1} , [where ν (nu) =wave number] and a band at 1656 cm^{-1} for the azomethine ($\text{C} \equiv \text{N}$) group, when complexes with vanadium (IV) in the presence of alcohol (ROH) the free nitrile was completely absent and hence the possibility of the guanlyl urea structure was ruled out. The decrease in $\nu(\text{C}=\text{N})$ on complexation indicates coordination of the

phenylamidine ($\text{C}=\text{N}$) group lowering the $\nu(\text{C}=\text{N})$ band to ca 1640 cm^{-1} , which is supported by lowering of the $\nu(\text{C}=\text{N})$ to ca 1667 cm^{-1} in all the complex is presumably due to a change in the $\text{C}=\text{N}$ band order, on coordination through the nitrogen atom, facilitated by transferred of electron density from the C-O-C bonded order is raised. The complexes show a ν_a (C-O-C) (ν_a =average wave number) stretch at ca 1180 cm^{-1} and ν_s (C-O-C) (stronger wave number) at ca 960 cm^{-1} .

The $\nu(\text{V}=\text{N})$ band appears at $430\text{-}420\text{ cm}^{-1}$. The spectra of all complexes show new bands around 970 cm^{-1} due to $\nu(\text{V}=\text{O})$ vibration. The presence of an ionic sulphate group in the complexes has been confirmed by the appearance of three bands at $140\text{ (V}_3\text{)}$, $960\text{ (V}_1\text{)}$ and $600\text{ cm}^{-1}\text{ (V}_4\text{)}$. The absence of V_2 band and none splitting of band indicate that the Td symmetry still holds.

3.2. Magnetic Moment

At room temperature, magnetic moments of the oxovanadium (IV) complexes lie in the range 0.855 BM to 1.4 BM. This suggests direct interaction between the metal ions which is responsible for the sub-normal magnetic moment value. It was inferred on the basis of magnetic data, that alcoholic oxygen might bridge the metal ions. This might be due to antiferromagnetic nature.

3.3. Magnetic Susceptibility Data

1. VO (AMUH) SO_4 .

Weight of sample (s)	1.68600
Temperature = 29°C	<u>1.61230</u>

$$\mu_{\text{eff}}\text{ (BM)} = 2.84 \sqrt{(\chi\text{M})} \text{ corr. } \chi\text{T}$$

$$= 0.855139265 \text{ BM.}$$

Where I_g = Intensity of magnetization,

H (G) = Strength of inducing magnetic field,

χ_g = Magnetic susceptibility,

$(\chi_g)_{\text{av}}$ = Average of magnetic susceptibility

2. VO (MAMUH) SO_4 .

Weight of sample (s)	1.63740
	<u>1.61225</u>

$$\mu_{\text{eff}}\text{ (BM)} = 2.84 \sqrt{(\chi\text{M})} \text{ corr. } \chi\text{T}$$

$$= 1.365789847$$

$$= 1.4 \text{ BM.}$$

3. VO (PhAMUH) $\text{SO}_4\cdot\text{H}_2\text{O}$.

Weight of sample (s)	1.70062
Temperature = 29°C	<u>1.67225</u>

$$\mu_{\text{eff}}\text{ (BM)} = 2.84 \sqrt{(\chi\text{M})} \text{ corr. } \chi\text{T}$$

$$= 0.926936427$$

$$= 1.0 \text{ BM.}$$

Table 2: IR Spectral Data of Oxovanadium (IV) Complex

Compound and colour	IR spectral Band (cm^{-1})	
	ν	$\nu(\text{SO}_4^{2-})$
VO(AMUH) SO_4 Light yellowish brown	1734 s	1080 s
	1696 s	948 vw
	1603 s	
VO(MAMUH) SO_4 Light brown	1754 s	1118 m
	1689 s	964 s
	1624 s	
VO(PhAMUH) $\text{SO}_4\cdot\text{H}_2\text{O}$ Yellowish brown	1724 s	1100 w
	1672 s	955 s
	1584 s	

Table 3: IR Data of Oxovanadium (IV) Complexes

Compounds and IR Spectral data	IR bands (cm^{-1})			
1. VO(AMUH) SO_4 Light yellowish brown	3380 s	3197s	1734 s	1696s
	1603 m	1455w	1357 m	1081s
	948 vw	615 m		
2. VO(MAMUH) SO_4 Light brown	3308 s	1754 s	1689 s	1624s
	1475 m	1916 m	1100 w	955s
	826 m			
3. VO(PhAMUH) $\text{SO}_4\cdot 3\text{H}_2\text{O}$ Yellowish brown	3290 s	1724 s	1672s	1584s
	1487 s	1325 m	1118m	964s
	830 m	750 m	613m	

(m= medium; s= strong; w= weak; vs= very strong; vw= very weak)

Table 4: Magnetic susceptibility of [VO (AMUH) SO_4]

Sample	Intensity of Mag.			I_g	$H(\text{G})$	χ_g	$(\chi_g)_{\text{av}}$
	Empty cup	Sample +cup	Corrected				
VO(AMUH) SO_4 Light yellowish Brown	-0.0022	-0.0026	0.0004	0.005427	8.010×10^3	0.677455×10^{-6}	0.72206533
	-0.0022	-0.0027	0.0005	0.006784	8.835×10^3	0.767884×10^{-6}	
	-0.0023	-0.0028	0.0005	0.006784	9.413×10^3	0.720733×10^{-6}	

Table 5: Magnetic susceptibility of [VO (MAMUH) SO₄]

Sample	Intensity of Mag.(I)			I _g	H(G)	χ _g	(χ _g) _{av}
	Empty cup	Sample +cup	Corrected				
VO(MAMUH)SO ₄ Light Brown	-0.0017	.0022	.0005	.0198807	8.010 x 10 ³	2.481986 x 10 ⁻⁶	2.2814 x 10 ⁻⁶
	-0.0018	-0.0023	.0005	.0198807	8.835 x 10 ³	2.2502 x 10 ⁻⁶	
	-0.0019	-0.0024	.0005	.0198807	9.413 x 10 ³	2.112048 x 10 ⁻⁶	

Table 6: Magnetic susceptibility of [VO (PhAMUH) SO₄] H₂O

Sample	Intensity of Mag.			I _g	H(G)	χ _g	(χ _g) _{av}
	Empty cup	Sample +cup	Corrected				
VO(PhAMUH)SO ₄ Yellowish brown	-0.0045	-0.0046	0.0001	0.003524	8.010x10 ³	0.677575x10 ⁻⁶	0.66230
	-0.0048	-0.0050	0.0002	0.007049	8.835x10 ³	0.797928x10 ⁻⁶	
	-0.0053	-0.0055	0.0002	0.007049	9.413x10 ³	0.748932x10 ⁻⁶	

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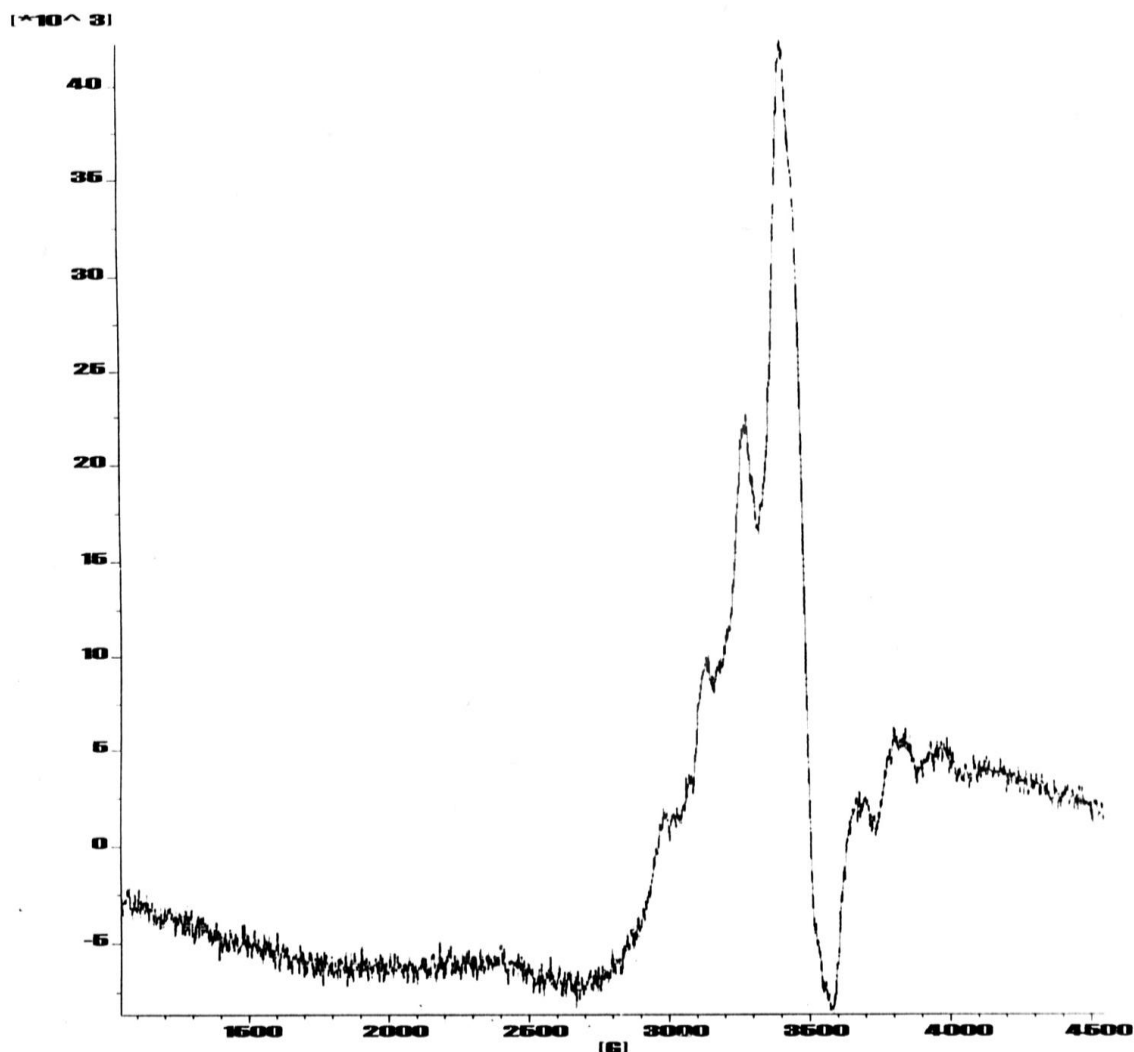


Fig. 1: EPR Spectra of [VO(AMUH)SO₄]

Filename :

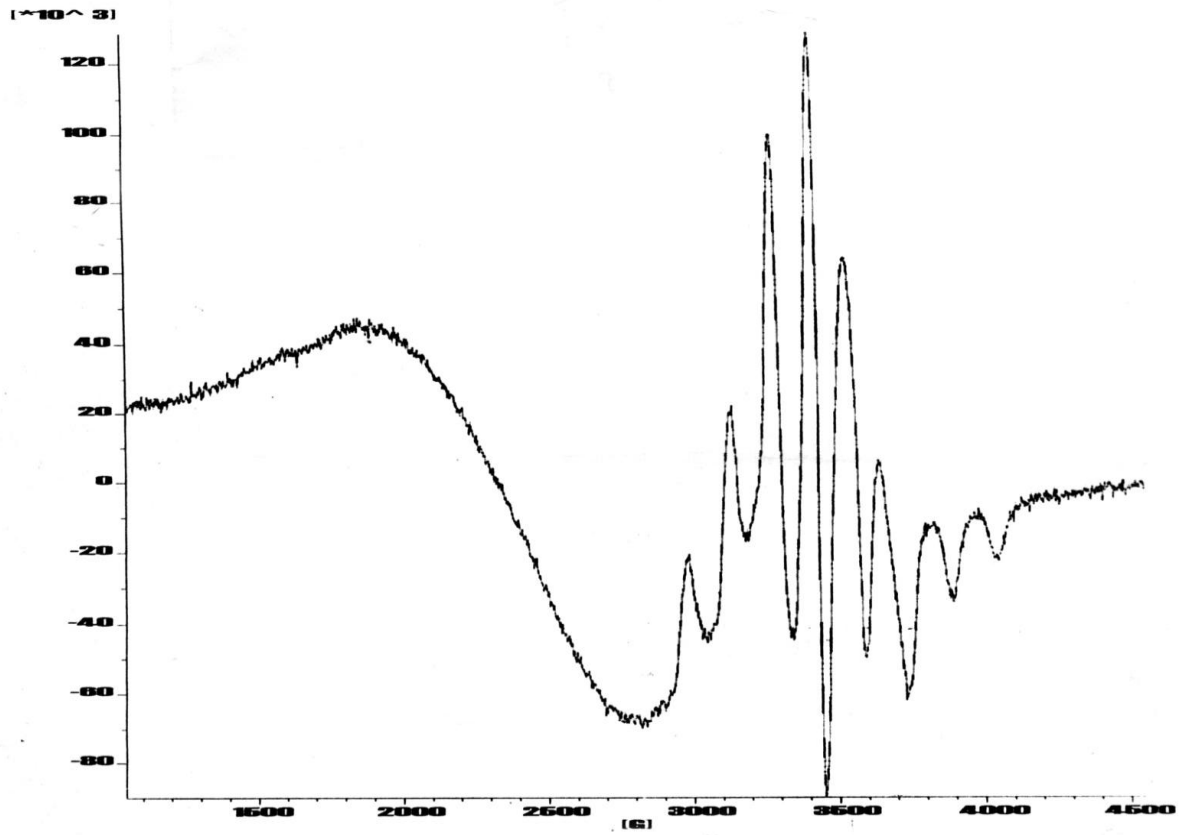


Fig. 2: EPR Spectra of [VO(MAMUH)SO₄]

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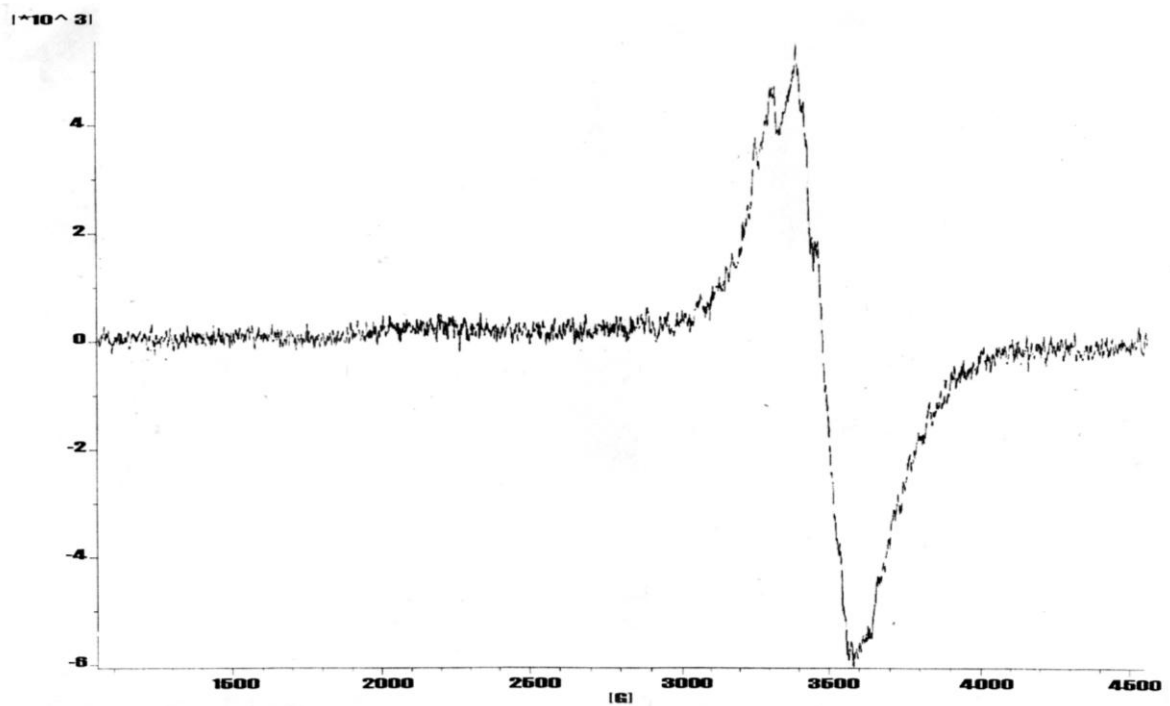


Fig. 3: EPR Spectra of [VO(phAMUH)SO₄.3H₂O]

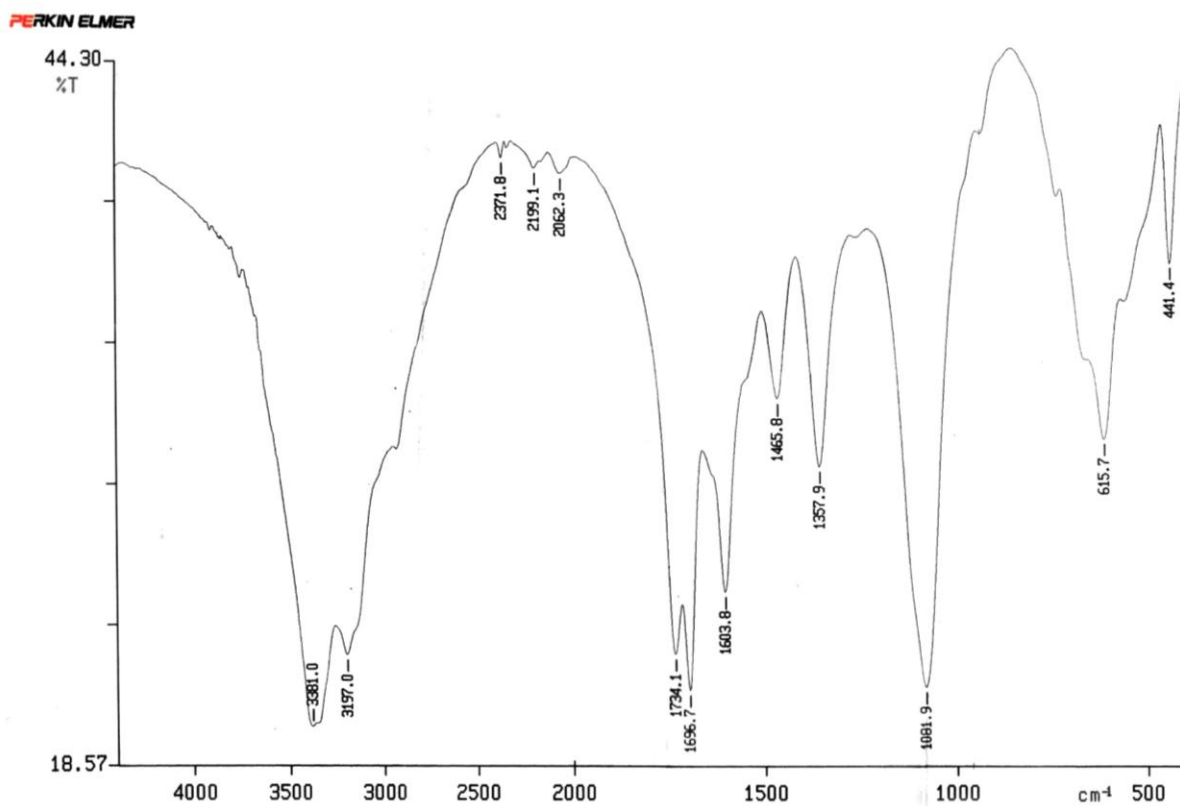


Fig. 4: IR Spectra of [VO(AMUH)SO₄]

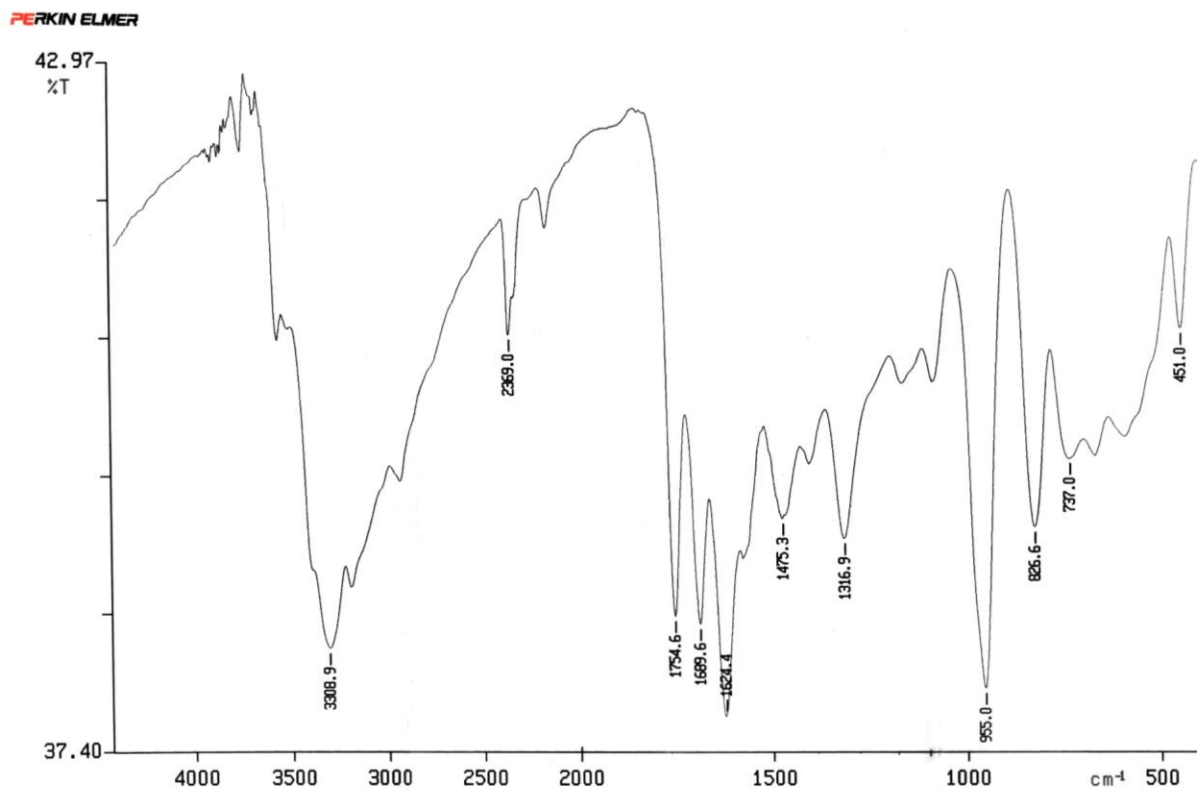


Fig. 5: IR Spectra of [VO(MAMUH)SO₄]

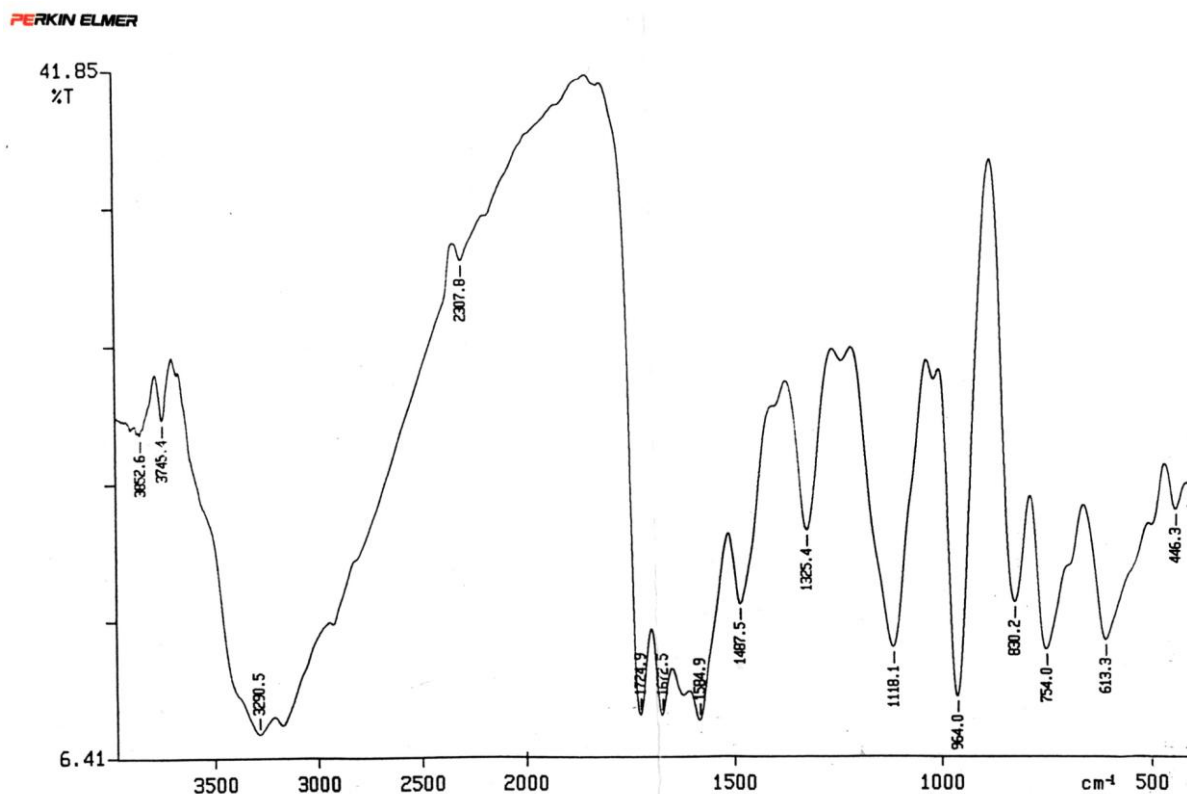
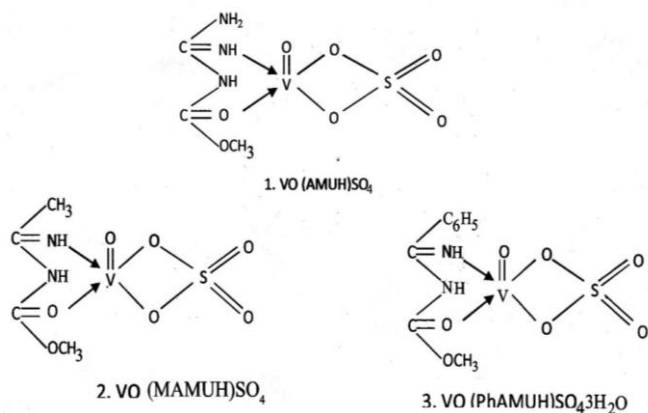


Fig. 6: IR Spectra of $[\text{VO}(\text{phAMUH})\text{SO}_4 \cdot 3\text{H}_2\text{O}]$

3.4. EPR Spectra

Since the complexes are insoluble, so we are taking only solid state EPR spectra. The X-band EPR spectra of oxovanadium (IV) complexes were recorded at room temperature and at liquid nitrogen temperature. The room temperature spectra exhibit eight lines due to hyperfine splitting of V, those nuclear spin number $i = 7/2$. The anisotropy is clearly visible in the spectra at liquid nitrogen temperature and bands are observed separately. Tentative structures of the complexes have been proposed of these compounds as.



4. CONCLUSION

The synthesis and characterization of oxovanadium complexes with dicyandiamide and substituted dicyandiamide was performed. Oxovanadium (IV) complexes were prepared by reacting vanadylsulphate monohydrate and different ligands in methanol. The IR spectra band for pure phenyldicyandiamide shows strong wave number and that of without phenyldicyandiamide decrease wave number which is due to a change in the $\text{C}=\text{N}$ bond order on coordination through the nitrogen atom, facilitated by transfer of electron density from $\text{C}-\text{O}-\text{C}$ bond order to raised. The magnetic moment of the compound lies between 0.85 BM to 1.4BM which suggested the directed interaction between ions. The present work will be helpful to undergo further research.

Conflict of interest

None declared

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