



PHYSICO-CHEMICAL INVESTIGATION ON SOME CARBODITHIOATE COMPLEXES OF OXOVANADIUM (IV)

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ABSTRACT: Some carbodithioate complexes of oxovanadium(IV) with general formulae: $[\text{VO}(4\text{-RPipzcdtH})_2\text{B}]\text{SO}_4$ and $[\text{VO}(4\text{-EtPipzcdt})_2\text{B}]$ (B = nil or Py, (R = M, Et and Pipzcdt = piperazine carbodithioate) have been prepared and characterized by elemental analysis, molar conductance, infrared, solution electronic absorption and proton NMR spectral, and room temperature magnetic susceptibility measurements. The oxovanadium (IV) complexes exhibit 1:1 electrolytic nature except $[\text{VO}(4\text{-EtPipzcdt})_2\text{B}]$ (B = Nil or Py) which exhibit non electrolytic nature. A square pyramidal geometry and presence of antiferromagnetic interactions for Zwitterionic and normal carbodithioate complexes of oxovanadium(IV), viz. $[\text{VO}(4\text{-RPipzcdtH})_2]\text{SO}_4$, $[\text{VO}(4\text{-EtPipzcdt})_2]$; and octahedral geometry for their pyridine adducts have been proposed.

Keywords: Oxovanadium (IV); dithiocarbamate; conductance; magnetic susceptibility.

INTRODUCTION

The early investigation on dithiocarbamates called as 1,1-dithiolato systems, which were performed several decades ago, centered around their use in agriculture as pesticides, vulcanization accelerators in rubber technology, high pressure lubricants and as analytical reagents.¹⁻⁴ They exhibit very rich coordination chemistry with a large variety of transition metals.⁵⁻⁹ Large volume of literature has been built up on dithiocarbamates for their use as pharmaceutical agents.¹⁰ The widely accelerating interest in complexes of these ligand systems now covers a varied area ranging from general considerations of metal-sulphur bonding and electron delocalization in transition metal complexes to potential their practical applications in these fields. The present investigations embody the derivatization of dithiocarbamate ligands from saturated heterocyclic secondary amines, viz. 1-methylpiperazine (1-MPipz) and 1-ethylpiperazine (1-Etpipz) and their complexation properties with oxovanadium (IV) metal ions.

MATERIAL AND METHODS

All the chemicals used were of analytical reagent grade and used as such. The ligands 4-methylpiperazine-1-carbodithioic acid (4-MPipzcdtH) and sodium-4-methylpiperazine-1-carbodithioate monohydrate (4-MpipzcdtNa.H₂O) were obtained by the methods as reported earlier¹¹. While the ligands 4-ethylpiperazine-1-carbodithioic acid (4-EtPipzcdtH) and sodium-4-ethylpiperazine-1-carbodithioate monohydrate (4-EtPipzcdtNa.H₂O) were prepared by the same method as was used for 4-MPipzcdtH and 4-MPipzcdtNa.H₂O.

1. Preparation of Complexes: Metal carbodithioate complexes reported under present investigation were synthesized by the following methods:

a) $\text{VO}(4\text{-EtPipzcdt})_2$ and $[\text{VO}(4\text{-RPipzcdtH})_2]\text{SO}_4$, (R =M, Et): To the methanolic solution of $\text{VO}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (.200 g; 0.79 mmol) kept at 40°C was added with stirring slightly less than stoichiometric amount of solid 4-EtPipzcdtNa (.320 g; 1.51 mmol) or solid 4-MPipzcdtH (.265 g; 1.506 mmol) or 4-EtPipzcdtH (.287g; 1.51 mmol), in small portions (~ 10 mg) after successive intervals of half an hour in a total period of ~12 hours. The grayish green coloured complex separated as the solid carbodithioic acid

dissolved. Centrifugation was done to avoid losses of the complex. Complex was washed several times with methanol using centrifugation technique and dried in CaCl₂ desiccator.

b) Pyridine (Py) Adducts of Vanadyl Carbodithioates: [VO(4-EtPipzcdt)₂ Py] and [VO(4-RPipzcdtH)₂Py]SO₄, (R= M, Et): To methanolic solution of pyridine (0.626 mmol) was added slightly less than the stoichiometric amount of solid metal complexes; VO(4-EtPipzcdt)₂ (0.626 mmol) or [VO(4-RPipzcdtH)₂]SO₄, (R= M, Et) in small portions (~10 mg) after successive intervals of half an hour in a total period of about 10 hours at 30⁰ C. The stirring was continued for another one hour when intense coloured complexes of the Lewis base separated out. Centrifugation was done to avoid losses of the complex. The complex was washed several times with methanol using centrifugation technique and dried in CaCl₂ desiccation.

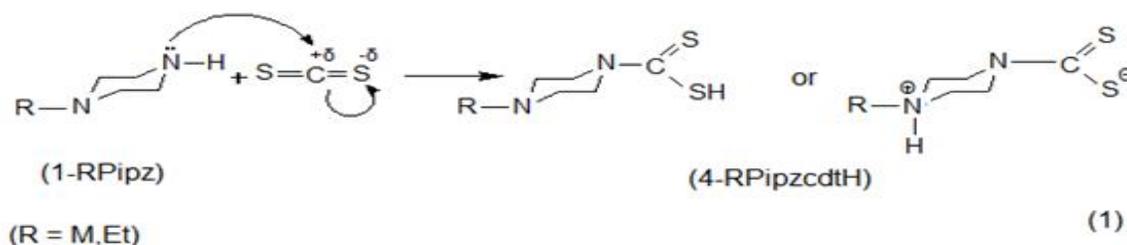
[Note: Both in solid and solution state the complexes are highly sensitive to moisture and so all the reactions were carried in a dry bag kept dried with CaCl₂]

2. Elemental Analysis: Carbon and hydrogen analyses were performed on an automatic Coleman-33 Analyzer while nitrogen was analysed by Kjeldahl's method. Vanadium and sulphur content in the complexes were determined gravimetrically as V₂O₅ and as barium sulphate respectively.

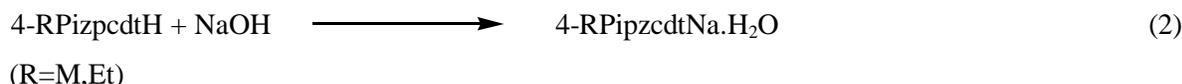
3. Physical Measurements: ¹H NMR spectra of the ligands and their complexes were recorded on JEOL JNM PMx60 SI spectrophotometer using (CD₃)₂SO as solvent and TMS as an internal standard. Infrared spectra of all the ligands and complexes were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4000-600 cm⁻¹ region, while Infrared spectrum of all the complexes were recorded as nujol mull with cesium chloride plates as windows in the 600-200 cm⁻¹ region. Ethanol/DMSO solution electronic absorption spectra of the complexes, with the solvent as the reference, in quartz glass cells were recorded on Cary 100 Bio UV- Visible recording Spectrophotometer (200-900 nm). Magnetic susceptibility measurements for the complexes were made on finely powdered samples using Gouy method. Molar conductances were obtained at 20 ±1⁰C using Elico Conductivity Bridge type CM – 82T.

RESULTS AND DISCUSSION

The carbodithioate ligand, 4-RpipzcdtH, (R=M, Et) obtained by insertion of CS₂ into the N-H bond of the heterocyclic amine, 1-Rpipz, (R=M, Et) exists as a Zwitterion (Eq. 1).

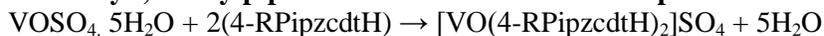


The sodium salt of 4-RPipzcdtH, (R=M, Et) has been obtained on addition of aqueous solution of NaOH to the solid carbodithioic acid (Eq 2).

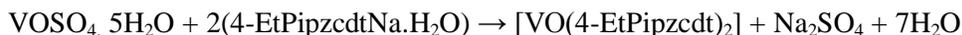


The synthesis of carbodithioate complexes of oxovanadium (IV) of the above mentioned ligands categorized into three types follow the reactions:

I. 4-Methyl-,4-Ethylpiperazine-1-carbodithioate Complexes of Oxovanadium(IV):



(R=M,Et)



II. Pyridine Adducts of 4-Methyl-, 4-Ethylpiperazine-1-carbodithioate Complexes of Oxovanadium (IV):



(R=M, Et)



Py = Pyridine

Table 1: Elemental Analytical Data and Physical Data of 4-Methyl, 4-Ethylpiperazine-1-carbodithioic Acids, Sodium salt of 4-Methyl, 4-Ethylpiperazine-1-Carbodithioic Acids and their Metal Complexes.

Sr. No.	Compound	Formula weight	Elemental Analysis Found (Calc.) %							Yield (%)	Decomposition Temp. °C	Colour
			C	H	N	S	O	M	Cl			
1.	4-MPipzcdtH C ₆ H ₁₂ N ₂ S ₂	176	40.43 (40.90)	6.32 (6.81)	16.15 (15.90)	35.90 (36.36)	---	---	---	98	200	creamish yellow
2.	4-EtPipzcdtH C ₇ H ₁₄ N ₂ S ₂	190	43.89 (44.21)	7.21 (7.37)	14.22 (14.74)	33.75 (33.68)	---	---	---	98	164	creamish yellow
3.	4-MPipzcdtNa.H ₂ O C ₆ H ₁₃ N ₂ S ₂ ONa	216	33.66 (33.33)	6.61 (6.02)	12.42 (12.96)	28.96 (29.43)	7.91 (7.41)	---	---	90	268	creamish yellow
4.	4-EtPipzcdtNa.H ₂ O C ₇ H ₁₅ N ₂ S ₂ ONa	230	37.74 (36.52)	6.12 (6.65)	13.21 (12.17)	27.44 (27.83)	6.42 (6.96)	---	---	90	242	creamish yellow
5.	[VO(4-MPipzcdtH) ₂] ₂ SO ₄ C ₁₂ H ₂₄ N ₄ S ₅ O ₅ V	515	28.42 (27.96)	4.83 (4.66)	10.43 (10.87)	31.46 (31.06)	14.90 (15.53)	9.70 (9.87)	---	92	250	grayish green
6.	[VO(4-EtPipzcdtH) ₂] ₂ SO ₄ C ₁₄ H ₂₈ N ₄ S ₅ O ₅ V	543	30.71 (30.94)	5.37 (5.16)	10.01 (10.31)	28.90 (29.46)	14.21 (14.73)	9.60 (9.38)	---	95	180	grayish green
7.	[VO(4-EtPipzcdt) ₂] C ₁₄ H ₂₆ N ₄ S ₄ O V	445	37.38 (37.75)	5.37 (5.84)	12.13 (12.58)	29.04 (28.78)	3.65 (3.59)	12.95 11.45	---	94	176	grayish green
8.	[VO(4-MPipzcdtH) ₂ Py] ₂ SO ₄ C ₁₇ H ₂₉ N ₅ S ₅ O ₅ V	594	34.14 (34.34)	4.92 (4.88)	11.32 (11.78)	25.70 (26.96)	13.19 (13.47)	9.01 (8.58)	---	96	110	intense green
9.	[VO(4-EtPipzcdtH) ₂ Py] ₂ SO ₄ C ₁₉ H ₃₃ N ₅ S ₄ O ₅ V	622	36.64 (36.65)	5.72 (5.31)	11.14 (11.25)	25.60 (25.72)	12.42 (12.86)	8.46 (8.19)	---	92	186	intense green
10.	[VO(4-EtPipzcdt) ₂ Py] C ₁₉ H ₃₁ N ₅ S ₅ O V	524	43.24 (43.51)	5.62 (5.92)	12.92 (13.36)	30.56 (30.33)	3.14 (3.04)	10.23 (9.72)	---	90	156	intense green

Infrared Spectral Studies: The IR spectra of free ligands 4-RpipzcdtH and 4-RPipzcdtNa.H₂O, (R=M, Et) (Table 2) show the (C[≡]N) stretching vibration at 1460-1412 cm⁻¹ which is in between a ν(C=N) band (1690-1640 cm⁻¹) and a ν(C-N) band (1360-1250 cm⁻¹), indicating a partial double bond character between carbon and nitrogen.¹² All the metal carbodithioates of oxovanadium(IV) and chromium(III) exhibit the ν(C[≡]N) at higher energies around 1495-1451 cm⁻¹ in comparison to free ligands. The rise in C[≡]N stretching frequency has been attributed to a considerable double bond character of the C[≡]N bond in the complexes.^{12,13} A shift (26-13 cm⁻¹) in ν(C[≡]N) values to lower wave number (1469-1451 cm⁻¹) in complexes of pyridine adducts of oxovanadium(IV) carbodithioates as compared to corresponding parent complexes has been observed. This reduction arises because of the relatively decreased electron flow of the nitrogen lone pair of electrons of NCS₂⁻ group towards the central metal ion. Since it also receives additional electron density from the new pyridine ligand. Observation of two bands in the region 1015-978 cm⁻¹ for the antisymmetric, ν_a(SCS) vibration and one band for the symmetric ν_s(SCS) stretch in the region 695-675 cm⁻¹ in all the complexes suggest the unsymmetrical chelating bidentate mode of coordination to metal ion¹⁴.

Table 2: Some coordinatively Diagnostic Features of Infrared Spectra (cm⁻¹) and Molar Conductance values, Λ_m (ohm⁻¹cm² mol⁻¹) of 4-Methylpiperazine -1-carbodithioic Acid, and their Metal Complexes.

Sr. No.	Compound	$\nu(\text{N-H})/(\text{O-H})$	$\nu(\text{C-H})$ (H ₃ C-N or H ₅ C ₂ -N)	$\nu(\text{CN})$	$\nu_a(\text{SCS})$	$\nu_s(\text{SCS})$	$\nu(\text{V=O})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$	$\nu(\text{M-N})$	Λ_m
1.	4MPipzcdtH	3600-3200 b,s	2850 s	1442 s	975 s	675 w	---	---	---	---	---
2.	4-EtPipzcdtH	3620-3230 b,s	2849 s	1448 s	990 s 978 m	672 w	---	---	---	---	---
3.	4-MPipzcdtNa.H ₂ O	3460-3160 b,s	2808 s	1455 s	989 s 971 m	686 w	---	---	---	---	---
4.	4-EtPipzcdtNa.H ₂ O	3465-3160 b,s	2818 s	1460 s	1015 m 997 s	680 w	---	---	---	---	---
5.	[VO(4-MPipzcdtH) ₂]SO ₄	3630-3250 b,s	2924 s	1464 s	1010 m 997 s	680 w	997	352	---	---	59
6.	[VO(4-EtPipzcdtH) ₂]SO ₄	3570-3280 b,s	2929 s	1449 s	1005 m 985 s	685 w	985	363	---	---	68
7.	[VO(4-EtPipzcdt) ₂]	---	2930 s	1490 s	1012 m 995 s	683 w	964	367	---	---	12
8.	[VO(4-MPipzcdtH) ₂]PySO ₄	3650-3230 b,s	2921 s	1451 s	1002 m 985 s	678 w	985	387	---	229	62
9.	[VO(4-EtPipzcdtH) ₂]PySO ₄	3655-3240 b,s	2928 s	1456 s	997 m 980 s	682 w	980	393	---	223	70
10.	[VO(4-EtPipzcdt) ₂]Py]	----	2925 s	1469 s	1018 m 992 s	680 w	962	399	----	219	10

Molar Conductance Studies: The molar conductance values of DMSO solutions of the oxovanadium(IV) carbodithioate complexes of present study, viz. [VO(4-RPipzcdtH)₂]SO₄ and [VO(4-RPipzcdtH)₂]PySO₄ (R = M, Et) lie in the range 59–70 ohm⁻¹cm² mole⁻¹ (Table 2) corresponding to 1:1 electrolytic behaviour.^{15,16} The molar conductance values of DMSO solutions of oxovanadium(IV) carbodithioates, viz. [VO(4-EtPipzcdt)₂] and [VO(4-EtPipzcdt)₂]Py fall in the range 10-15 ohm⁻¹cm² mole⁻¹ which is indicative of non electrolytic nature of these complexes.

Proton NMR Spectral Studies: ¹H NMR data (δ ppm) of 1-EtPipz, 4-EtPipzcdtH (in D₂O) and Zwitterionic complexes, viz. [VO(4-EtPipzcdtH)₂]SO₄, [VO(4-EtPipzcdtH)₂]PySO₄, as well as normal carbodithioate complexes, viz. [VO(4-EtPipzcdt)₂], [VO(4-EtPipzcdt)₂]Py, (all in (CD₃)₂SO) throws more light regarding the formation of 4-ethylpiperazine-1-carbodithioic acid and its bonding to a central metal ion. Heterocyclic saturated secondary amine, i.e. 1-EtPipz exhibits resonance signals for N-H proton at δ 2.40, -CH₂⁻ heterocyclic ring protons at δ 2.36, -CH₂- protons of H₃C-H₂C-N< group around δ 2.31-2.35 and -CH₃ protons of H₃C-H₂C-N< group around δ 0.95-0.98 ppm. The proton NMR spectrum of free acid ligand, 4-EtPipzcdtH shows the resonance signals: two overlapping triplets at δ 2.49, a quartet around δ 2.38-2.43 and a triplet around δ 1.00-1.03 ppm corresponding to four -CH₂- (2,3,5 and 6), -CH₂-protons of H₃C-H₂C-N< and -CH₃ protons of H₃C-H₂C-N< group respectively (Figure1)

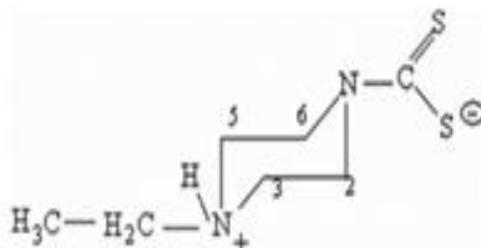


Figure 1: Zwitterionic Form of 4- EtPipzcdtH Ligand.

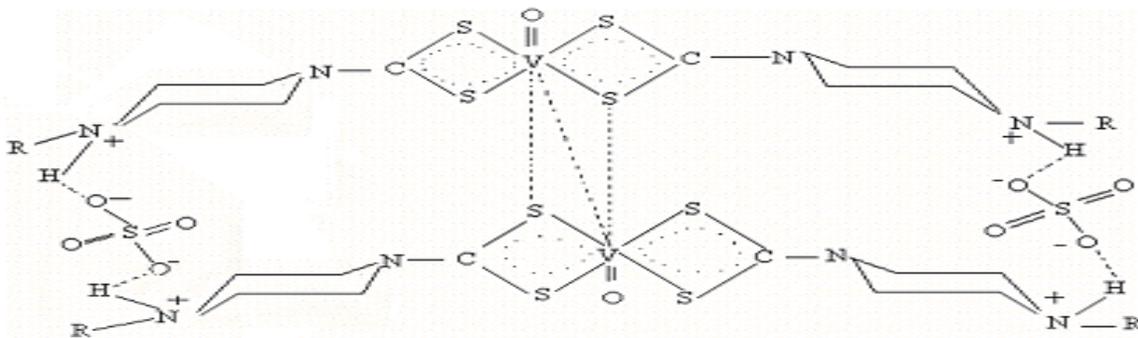
Table 3: ¹H NMR Spectral Data, δ(ppm) for 1-Ethylpiperazine, 4-Ethylpiperazine-1-carbodithioic Acid and some Oxovanadium(IV) Carbodithioate Complexes.

Sr. No.	Compound	NH	(3,5-)CH ₂	(2,6-)CH ₂	CH ₂ (C ₂ H ₅)	CH ₃ (C ₂ H ₅)	CH
1.	1-EtPipz	2.40(s,1H)	2.36(t,8H:2,3,5and 6-CH ₂)		2.31-2.35 (q, 2H)	0.95-0.98 (t, 3H)	---
2.	4-EtPipzcdtH	4.30(s,1H)	2.49(t,8H:2,3,5and 6-CH ₂)		2.38-2.43 (q, 2H)	1.00-1.03 (t, 3H)	---
3.	[VO(4-EtPipzcdtH) ₂]SO ₄	4.25(s,1H)	3.91-3.98 (t, 4H)	1.25-1.30 (t, 4H)	2.46-2.57 (q,2H)	1.09-1.15 (t,3H)	---
4.	[VO(4-EtPipzcdt) ₂]	---	3.37-3.40 (t, 4H)	1.12-1.13 (t, 4H)	2.48-2.59 (q, 2H)	1.01-1.11 (t, 3H)	---
5.	[VO(4-EtPipzcdtH) ₂ Py]SO ₄	4.32(s, 1H)	3.86-3.93 (t, 4H)	1.14-1.24 (t, 4H)	2.54-2.92 (q, 2H)	1.03-1.26 (t, 3H)	7.35 (t, 1H: 3, 5-CH) 7.75 (t, 1H: 4-CH) 8.56 (d,1H: 2,6-CH)

Disappearance of signal due to >N-H proton corresponding to free 1-EtPipz suggests, the formation of 4-EtPipzcdtH ligand on its reaction with carbon disulfide. Appearance of a new signal at δ 4.30 ppm has been attributed to proton resonance of N-H as a result of formation of a new N-H bond (Figure1). ¹H NMR spectra of oxovanadium(IV) carbodithioates (Table 3), exhibiting separate triplets due to 2,6-methylene (δ1.12-1.30 ppm) and 3,5 – methylene (δ 2.58- 3.98 ppm) have been observed on the upfield and downfield sides respectively in comparison to the free-ligand. Johnson ¹⁷ has indicated that the double band character of the C-N band should result in hindered rotation of the S₂C=N group. Resolution of the two above said signals in the ¹H NMR spectra of the complexes under study in comparison to free acid may result because of the hindered rotation of the S₂C=N group of the 4-EtPipzcdtH ligand. The observation of δ 2,6 –CH₂ on high field side has plausibly been attributed to paramagnetic behaviour of oxovanadium(IV) (d¹) system.¹⁸ Coordination of the carbodithioate ligand to the metal ion has been found to cause a shielding of 2,6-methylene protons with increase in δ value of the order of δ 1.19-1.37 ppm, and deshielding of 3,5 protons with downfield shift of the order of δ 0.09-1.48 ppm.

Magnetic Susceptibility Studies: For the Zwitterionic and normal carbodithioate complexes, viz. [VO(4-RPipzcdtH)₂]SO₄ (R = M, Et), [VO(4-EtPipzcdt)₂] the calculated room temperature μ_{eff} values are found to lie in the range 1.70-1.58 B.M (Table 4). The μ_{eff} values in these complexes are subnormal since these are less than those for magnetically dilute oxovanadium (IV) complexes (μ_{eff}^{S.O.} value for one unpaired electron = 1.73 B.M.). The observed values, however, fall in the range of the values reported for binuclear oxovanadium (IV) complexes in which direct spin-spin interaction between the two metal ions has been proposed.^{19,20} The magnetic moment values for the present oxovanadium(IV) complexes may be ascribed to the presence of the spin-exchange coupling phenomenon called antiferromagnetism.

The possibility of the occurrence of indirect or super exchange interaction mechanism for antiferromagnetism in these complexes seems to be more probable and the super exchange interaction may result from the bridging carbodithioate ligands. This bridge and other features of the structure of [VO(4-RPipzcdtH)₂]SO₄ (R = M, Et) inferred from the studies mentioned above, get included if we assign this complex the structure as shown in Figure 2.



[R = M, Et]

Figure 2: structure of [VO(4-RPipzcdtH)₂]SO₄ (R = M, Et).

The room temperature magnetic moments for the complexes, viz. [VO(4-RPipzcdtH)₂Py]SO₄ (R=M, Et) and [VO(4-EtPipzcdt)₂Py] lie in the range 1.90-1.80 B.M.. These complexes have [VS₄NO] chromophore indicative of coordination number six around vanadium atom corresponding to octahedral stereochemistry.

Electronic Absorption Spectral Studies: The DMSO solution electronic absorption spectra of the complexes [VO (4-RPipzcdtH)₂]SO₄ (R = M, Et), [VO(4-EtPipzcdt)₂] exhibit three well-defined bands in the regions (I) 12,125-11,900 , (II) 17,800-16,950 , (III) 28,570-24,570 cm⁻¹. The bands (I) and (II) are assigned to the d-d transitions: (I) b₂(d_{xy}) → e*_{II} (d_{xz}, d_{yz}) and (II) b₂ (d_{xy}) → b₁* (d_{x²-y²) characteristic of coordination number six around vanadium atom. The third band (III) is assigned as b₂ (d_{xy}) → a₁* (d_{z²)^{21,22,23}. The absorption spectra of complexes, viz. [VO(4-RPipzcdtH)₂Py]SO₄ (R=M,Et) (Figure 3) and (VO(4-EtPipzcdt)₂Py) exhibit a broad weak band in the region (13,795-13,335), (12,195-11,673) cm⁻¹. This band has been attributed to the transition ²E_g ← ²T_{2g} in octahedral d¹ system and shows signs of double structure, presumably due to the splitting of the ²E_g term by a low symmetry ligand field component.}}

Table 4: Electronic Absorption Spectra (cm⁻¹) and μ_{eff} Values of Transition Metal 4-Methyl- and 4-Ethylpiperazine-1-carbodithioate Complexes.

Sr. No.	Compound	b ₂ (d _{xy})→a ₁ * (d _{z²)}	b ₂ (d _{xy})→b ₁ * (d _{x²-y²)}	b ₂ (d _{xy})→e* _{II} (d _{xz} , d _{yz})	μ _{eff} (B.M.)
1.	[VO(4-MPipzcdtH) ₂]SO ₄	28,570	17,800	12,125	1.58
2.	[VO(4-EtpipzcdtH) ₂]SO ₄	26,450	17,000	11,975	1.70
3.	[VO(4-Etpipzcdt) ₂]	24,570	16,950	11,900	1.68
4.	[VO(4-MPipzcdtH) ₂ Py]SO ₄		² E _g ← ² T _{2g} 13,795 12,195		1.80
5.	[VO(4-EtPipzcdtH) ₂ Py]SO ₄		13,515 11,765		1.88
6.	[VO(4-EtPipzcdt) ₂ Py]		13,335 11,673		1.90

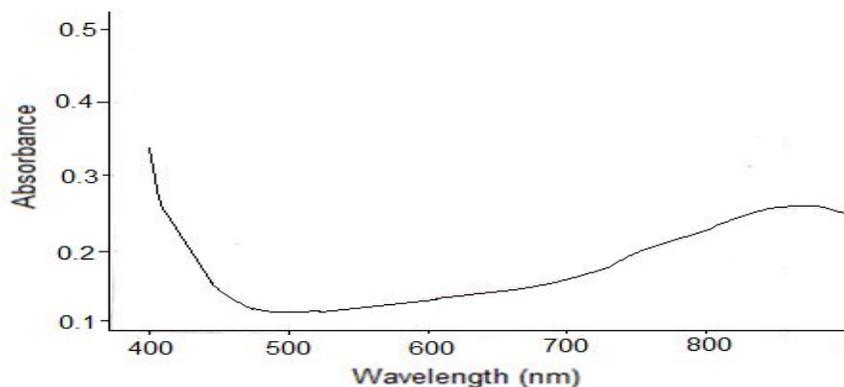


Figure 3: Electronic absorption spectra of $[\text{VO}(\text{4-EtPipzcdtH})_2\text{Py}]\text{SO}_4$.

CONCLUSION

Present investigation involves the synthesis of and studies on oxovanadium (IV) complexes with general formulae: $[\text{VO}(\text{4-RPipzcdtH})_2\text{B}]\text{SO}_4$ and $[\text{VO}(\text{4-EtPipzcdt})_2\text{B}]$ (B = nil or Py, (R = M, Et and Pipzcdt = piperazine carbodithioate). The molar conductance values reveal the 1:1 electrolytic nature for oxovanadium (IV) complexes except $[\text{VO}(\text{4-EtPipzcdt})_2\text{B}]$ (B = Nil or Py) which exhibit non electrolytic nature. Magnetic and solution electronic absorption spectral data suggests square pyramidal geometry and presence of antiferromagnetic interactions for Zwitterionic and normal carbodithioate complexes of oxovanadium(IV), viz. $[\text{VO}(\text{4-RPipzcdtH})_2]\text{SO}_4$ (R = M, Et), $[\text{VO}(\text{4-EtPipzcdt})_2]$; and octahedral geometry for their pyridine adducts, viz. $[\text{VO}(\text{4-RPipzcdtH})_2\text{Py}]\text{SO}_4$ (R = M, Et), $(\text{VO}(\text{4-EtPipzcdt})_2\text{Py})$.

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REFERENCES

1. Singhal, S., Garg, A. N. and Chandro, K. (2004) *J. Therm. Anal. Cal.*, 78, 941.
2. Sharma, A. K. (1986) *Thermochim. Acta*, 104, 339.
3. Hill, J. O., Murray, J. P. and Patil, K. C. (1994) *Rev., Inorg. Chem.*, 14, 363.
4. Zhang, T. H., Shan, X. Q., Liu, R.X., Tang, H. X., Zhang, S. Z. (1998) *Anal. Chem.*, 70, 3964.
5. Victoriana, L.I., Coord. (2000) *Chem. Rev.*, 196, 383.
6. Lim, P. J., Cook, V. C., Doonam, C. J., Young, C. J. and Tiekink, E. R. T. (2000) *Organomet.*, 19, 5643.
7. Garje, S. S. and Jain, V. K., Coord (2003) *Chem. Rev.*, 236, 35.
8. Van Koningsbruggen, P. J., Maeda, Y. and Oshio, H. (2004) *Top. Curr. Chem.*, 233, 259.
9. Ivanov, A.V. and Antizutkin, O. N. (2005) *Top. Curr. Chem.*, 246, 271.
10. Mauclaire, Laurent, Serthommier, Eric. F. R. *Apple.*, 15, 416(2000).
11. Kalia, S. B., Kaushal, G., Lumba, K. and Priyanka (2008) *J. Therm. Anal. Calorim.*, 91(2), 609-613.
12. Siddiqi, K. S., Shahab A. A. (2005) Nami and Lutfullah, *Synthesis and Reacivity in Inorganic, Metal-Organic and Nano- Metal Chemistry*, 35, 445-451.
13. Eisemberg, R. (1970) *Progr Inorg. Chem.*, 12, 295.
14. Bonati, F. and Ugo, R., J. (1967) *Organomets. Chem.*, 10, 257.

15. Geary, W.J. (1971) *Coord. Chem. Rev.*, 7, 81.
16. Chohan, Z. H., Sumrra, S. H., Youssoufi, M. H. and Hadda, T. B. (2010) *Eur. J. Medici. Chem.*, 45, 2739-2747.
17. Johnson, B. F. G. and Al. Abaidi, K. H., (1968) *Commun.*, 876.
18. Drago, R. S., (1978) *Physical Methods in Inorganic Chemistry*.
19. Zelentsov, V. V., Dokl, Akad. N. (1961) *USSR*, 139, 1110.
20. Zelentsov, V. V., Russ. (1962) *J. Inog. Chem.*, 7, 670.
21. Singh, A.K., Puri, B.K. and Rawelly, R.K., (1988) *Ind. J.Chem.*, 27(A), 430.
22. Doadrio, A. L., Sotelo, J. and Ruano A.F., (2002) *Quim. Nova*, 25(4), 1120.
23. Mishra, A. P. and Pandey, L. R., Indian, (2005) *J. Chem.*, 44A. 1803.