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Synthesis, spectral, thermal and biological properties of some novel coordination compounds of VO(IV) and biological 4[N-(4'-ethylbenzalidene) amino] antipyrine thiosemicarbazone and 4[N-(2', 4'-dimethyl benzalidene amino) antipyrine thiosemicarbazone

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Abstract

In present studies the synthesis, characterization and biological properties of oxovanadium(IV) coordination compounds of 4[N-(4'-ethylbenzalidene)amino] antipyrine thiosemicarbazone (EBAAPTS) and 4[N-(2',4'-dimethylbenzalidene)amino] antipyrine thiosemicarbazone (DMBAAPTS) with the general composition VOX₂L (X = Cl⁻, Br⁻, I⁻, NO₃⁻ or NCS⁻) and VO(ClO₄)₂(L)H₂O (L = EBAAPTS or DMBAAPTS) are described. All the complexes were characterized by elemental analyses, molar mass, molar conductance, magnetic susceptibility, infrared and electronic spectra. In all these complexes, both the thiosemicarbazones behave as neutral tridentate (N, N, S) ligands. The thermal properties of the representative complexes are also reported. The most probable geometry of the complexes is proposed.

Keywords: Oxovanadium (IV) complexes; Thiosemicarbazone; Biological activity; Mixed ligand complexes.

1. Introduction

Due to structural versatility of transition metal-complexes of Schiff bases, a number of workers [1-8] have reported schiff base complexes of oxovanadium(IV), interest in the study of thiosemicarbazones has been growing because of their wide spectrum of medicinal and biological properties [9-12]. In view of the versatile importance of N, N, S-containing thiosemicarbazones [13], it is worthwhile to synthesize some oxovanadium (IV) complexes of 4[N-4'-(ethylbenzalidene)amino] antipyrine thiosemicarbazone (EBAAPTS) and 4[N-(2',4'-dimethylbenzalidene)amino] antipyrine thiosemicarbazone (DMBAAPTS) (Fig 1a and 1b).

2. Experimental

Oxovanadium(IV) chloride and bromide were prepared by reported method [14]. Oxovanadium(IV) perchlorate was prepared by the method of Sathyanarayana and Patel [15].

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Oxovanadium (IV) iodide in solution was prepared by treating an ethanolic solution of VOCl_2 with KI in 1:2 equimolar ratio and the reaction mixture stirred on a magnetic stirrer for about 1hr. The precipitated KCl was filtered off and the filtrate containing VOI_2 was used for complexation. Oxovanadium(IV) thiocyanate solution was prepared by the treating an aqueous solution of oxovanadium(IV). The clear blue filtrate obtained after removal of the solid was concentrated by passing dry air when syrupy green solution was obtained. Oxovanadium(IV) nitrate was prepared by treating solution of oxovanadium(IV) chloride with silver nitrate solution.

Both the ligands *i.e.* EBAAPTS and DMBAAPTS were synthesized and characterized by reported method [13].

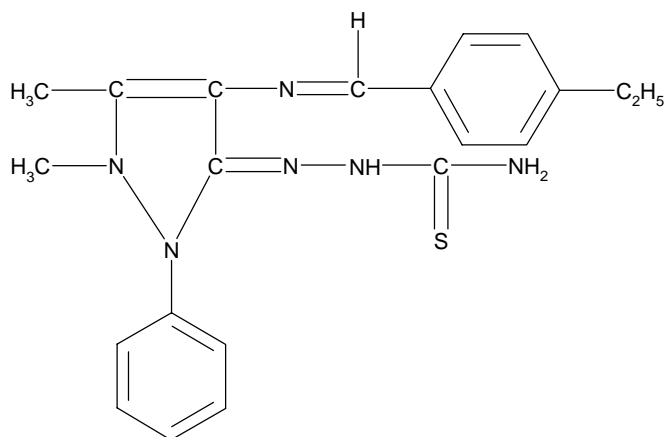


Fig. 1a. Structure of 4[N-(4'-Ethybenzalidene)amino] antipyrine thiosemicarbazone (EBAAPTS).

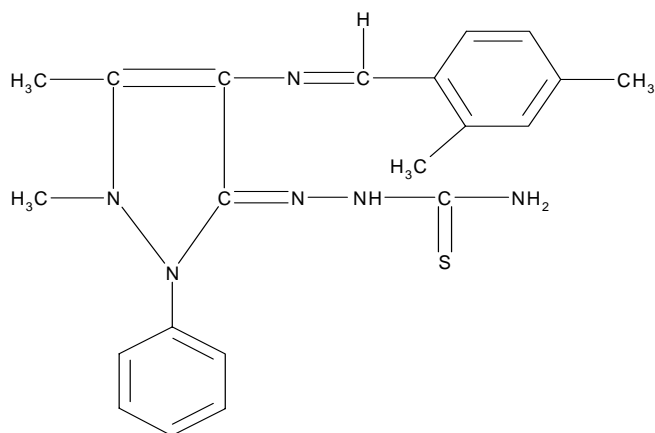


Fig. 1b. Structure 4[N-(2',4'-Dimethylbenzalidene)amino] antipyrine thiosemicarbazone (DMBAAPTS).

2.1. Synthesis of complexes

All the oxovanadium(IV) complexes of thiosemicarbazones were synthesized by the following general method. Methanolic solution of the respective ligand was mixed with a hot aqueous ethanolic solution of the corresponding oxovanadium(IV) salt (in 1:1 molar ratio). The reaction mixture was refluxed on a water bath for is 2 hr. The solvent was partially distilled off and the mixture was cooled at room temperature. The separated precipitates were suction filtered, washed with cold ethonol and dried in vacuo at room temperature over P_4O_{10} .

2.2. Analytical techniques

Vanadium was estimated by igniting the complexes in air and weighing as V_2O_5 . The halogens were estimated by Volhard's method [16]. The thiocyanate was estimated by titrating slightly acidic solution of the complex with standard silver nitrate solution. The perchlorate was estimated by the method suggested by Kurz *et al.* [17]. Sulphur was estimated gravimetrically as $BaSO_4$. The percentage of nitrogen was determined by Kjeldahl's method. The conductivity measurement was carried out using Toshniwal conductivity bridge CL01/01 and a dip type cell operated at 220 volts A.C. mains. All the measurements were made at room temperature in $PhNO_2$. The molecular weight of the complexes was determined cryoscopically in $PhNO_2$ using a Beckmann thermometer. The magnetic susceptibility of these complexes were determined at room temperature using Gouy balance and anhydrous copper(II) sulphate as calibrant. Infrared spectra in the range $4000-200\text{ cm}^{-1}$ of these complexes were recorded on a Perkin Elmer FT-IR spectrophotometer model spectrum 1000 in KBr. Electronic spectra were recorded at room temperature on a GBC (Australia) UV-visible spectrophotometer Cintra 5. Thermogravimetric analyses of the complexes were carried out in static air with open sample holder and a small platinum boat at the heating rate of $6\text{ }^\circ\text{C min}^{-1}$.

Antibacterial activity was done by the paper-disc plate method. The nutrient agar medium (peptone, calf extract, NaCl and agar-agar) and paper discs (Whatman No.1) were used. The compounds were dissolved in DMF in 500 and 1000 ppm concentrations. The filter paper discs were soaked in different solutions of the compounds, dried and then placed in the petri dishes previously seeded with the test organisms (*Escherichia coli* and *Klebsiella aerogenus*). The plates were incubated for 24-30 hr at $28 \pm 2\text{ }^\circ\text{C}$ and the inhibition zone around each disc was measured. The antifungal activity was evaluated against *Fusarium oxysporum* and *macrophomina phaseolina*, using standard food poisoning technique and a procedure recommended for testing new chemicals [18]. The linear growth of the fungus was recorded by measuring the diameter of the fungus colony after 96 hr and the percentage inhibition was calculated as $100(C-T)/C$, where C and T are the diameters of the fungus colony in the control and test plates, respectively.

3. Results and discussion

An ethanolic solution of VO(IV) salts on treatment with EBAAPTS or DMBAAPTS form complexes of the general composition VOX_2L ($X = Cl^-, Br^-, I^-, NO_3^-$ or NCS^-) or $VO(ClO_4)_2(L)H_2O$ ($L = EBAAPTS$ or $DMBAAPTS$). The analytical data of these complexes are given in Table 1. All the complexes are fairly stable and can be stored for long period at room temperature. The complexes are generally soluble in common organic solvents. The molar conductance values of all the complexes in $PhNO_2$ at room temperature are presented in Table 1. The molar conductance values of oxovanadium(IV) are in consistent with 1:1 electrolytic nature of the halo, pseudohalo complexes while perchlorato complexes are 1:2 electrolytes [19]. The molecular weight of the complexes as determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance data shown in Table 1.

The magnetic moments of the VO(IV) complexes are reported in Table 1. The magnetic moments of the complexes were found to be in 1.72-1.83 BM range. These magnetic moments are close to "spin only" values expected for $3d^1$ VO(IV) complexes with normal magnetic properties [19, 20].

3.1. Infrared spectra

A study and comparison of infrared spectra of free ligands (EBAAPTS and DMBAAPTS) and their VO(IV) complexes (Table 2 and 3) imply that these thiosemicarbazones behave as neutral tridentate (N, N, S) and the central metal VO(IV) is surrounded by N and N of two

azomethine groups and of S of thioketo group. The strong bands observed at 3380-3205 cm^{-1} region in the free ligands have been assigned to $\nu(\text{N-H})$ vibrations. There is no change in these frequencies observed after complexation. Thus the possibility of complexation at this group is precluded. The absorptions at 1608-1612 cm^{-1} in these thiosemicarbazones is assigned to $\nu(\text{C=N})$ vibrations of imine nitrogen, which is in agreement with the observations of previous workers [21, 22].

Table 1

Analytical, conductivity, molecular weight and magnetic moment data of VO(IV) complexes of thiosemicarbazones

Complexes	Yield (%)	Analysis: Found (%)				M.wt. Found	Λ_m $\text{ohm}^{-1}\text{cm}^2$ mol^{-1}	μ_{eff} (BM)
		V	N	S	Anion			
$\text{VOCl}_2(\text{EBAAPTS})$	80	9.56 (9.62)	15.74 (15.84)	5.96 (6.03)	13.28 (13.39)	262 (530)	30.1	1.76
$\text{VOBr}_2(\text{EBAAPTS})$	82	9.17 (8.23)	13.48 (13.57)	5.10 (5.16)	25.77 (25.84)	307 (619)	24.9	1.81
$\text{VOI}_2(\text{EBAAPTS})$	78	7.08 (7.15)	11.69 (11.78)	4.40 (4.48)	35.51 (35.62)	354 (713)	23.8	1.79
$\text{VO}(\text{NO}_3)_2(\text{EBAATS})$	80	8.67 (8.74)	19.11 (19.21)	5.43 (5.48)	—	289 (583)	24.3	1.72
$\text{VO}(\text{NCS})_2(\text{EBAAPT})$	72	8.80 (8.86)	19.34 (19.47)	16.51 (16.69)	20.06 (20.17)	284 (575)	239	1.80
$\text{VO}(\text{ClO}_4)_2(\text{EBAAPT}) \cdot \text{H}_2\text{O}$	70	7.48 (7.54)	12.31 (12.42)	4.68 (4.73)	29.28 (29.43)	222 (676)	52.9	1.79
$\text{VOCl}_2(\text{DMBAAPTS})$	78	9.56 (9.62)	15.73 (15.84)	5.95 (6.03)	13.27 (13.39)	263 (530)	29.3	1.78
$\text{VOBr}_2(\text{DMBAAPTS})$	80	8.18 (8.23)	13.48 (13.57)	5.11 (5.16)	25.74 (25.84)	308 (619)	28.2	1.80
$\text{VOI}_2(\text{DMBAAPTS})$	81	7.07 (7.15)	11.68 (11.78)	4.40 (4.48)	35.52 (35.62)	355 (713)	25.6	1.78
$\text{VO}(\text{NO}_3)_2(\text{DMBAAPTS})$	79	8.68 (8.74)	19.10 (19.21)	5.39 (5.48)	—	288 (583)	24.1	1.83
$\text{VO}(\text{NCS})_2(\text{DMBAAPTS})$	81	8.81 (8.86)	19.35 (19.47)	16.58 (16.69)	20.07 (20.17)	284 (575)	25.0	1.78
$\text{VO}(\text{ClO}_4)_2(\text{EBAAPTS})\text{H}_2\text{O}$	70	7.47 (7.54)	12.30 (12.42)	4.68 (4.73)	29.29 (29.43)	224 (676)	53.2	1.81

On complexation, these frequencies were observed to be shifted to lower wave number (Table 2 and 3). These observations suggest the involvement of unsaturated nitrogen atoms of two azomethine groups in bonding with the metal ion. In substituted thioureas, the (C=S) stretching vibrations show much contribution from some other vibrations such as (CN) stretching and banding, as well as (N-C-S) bending modes [23]. In the spectra of present ligands, the bands observed in 1295-1260 cm^{-1} , 1130-1080 cm^{-1} and 840-760 cm^{-1} region are assigned to [$\nu(\text{C=S}) + \nu(\text{C=N}) + \nu(\text{C-N})$] and (N-C-S) + $\delta(\text{C=S})$ bending and $\nu(\text{C=S})$ stretching respectively, following the observations of Swaminathan and Irving [24] and some other researches [25]. Coordination of sulphur with the metal ion would result in the displacement of electrons toward the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation (C=S) stretching vibrations should decrease and that of (CN) should increase [25]. In all the present complexes of VO(IV) with EBAAPTS and DMBAAPTS, the frequencies in the range 1295-1260 and 1130-1080 cm^{-1} get an increase by nearly 40-50 cm^{-1} . Similarly bending modes of (N-C-S) and (C=S) also get an increase but in lesser amount. On the other hand, on complexation the frequencies in 840-760

cm^{-1} are shifted to lower wave numbers and intensity of the bonds is also reduced. All these peculiar changes on complexation confidently preclude any unambiguous confirmation of a (V-S) bond. The possibility of thione-thiol tautomerism ($\text{H}-\text{N}-\text{C}=\text{S}$) \rightleftharpoons ($\text{C}=\text{N}-\text{SH}$) in these ligands has been ruled out, because no bands around $2700\text{-}2500\text{ cm}^{-1}$, which are characteristic of the thiol group are displayed in the infrared spectra [26].

Table 2Key Infrared bands (cm^{-1}) of oxovanadium(IV) complexes of EBAAPTS.

Assignments	EBAAPTS	VOCl_2 (EBAAPTS)	VOBr_2 (EBAAPTS)	VOI_2 (EBAAPTS)	$\text{VO}(\text{NO}_3)_2$ (EBAAPTS)	$\text{VO}(\text{NCS})_2$ (EBAAPTS)	$\text{VO}(\text{ClO}_4)_2$ (EBAAPTS) H_2O
$\nu(\text{NH})$	3380 s 3290 s	3382 s 3290 s	3380 s 3287 m	3385 s 3292 s	3382 s 3290 s	3380 s 3291 s	3382 s 3292 s
$\nu(\text{C}=\text{N})$	1612 vs	1570 s	1568 s	1572 s	1565 s	1560 s	1563 s
$\nu(\text{C}=\text{S})+$ $\nu(\text{C}=\text{N})+$ $\nu(\text{C}-\text{N})$	1295 s 1270 vs	1340 s 1283 m	1342 s 1282 m	1350 s 1220 m	1345 s 1292 m	1342 s 1290 m	1345 s 1265 m
$\delta(\text{NCS})+$ CS bending	1130 s 1080 m	1170 m 1115 m	1173 m 1110 m	1170 m 1113 m	1172 m 1125 m	1170 m 1120 m	1175 m 1115 m
$\nu(\text{N}-\text{N})$	1050 m	1062 m	1065 m	1060 m	1062 m	1065 m	1060 m
$\nu(\text{V}=\text{O})$ oxocation	—	982 m	963 m	965 m	970 m	960 m	972 m
$\nu(\text{C}-\text{S})$	840 s 760 vs	878 m 712 m	875 m 710 m	872 m 715 m	875 m 720 m	870 m 718 m	872 m 722 m
$\nu(\text{V}-\text{N})$ $\nu(\text{V}-\text{S})$	—	442 m 345 m	445 m 352 m	442 m 350 m	445 m 345 m	440 m 342 m	445 m 352 m

Table 3Key Infrared bands (cm^{-1}) of oxovanadium(IV) complexes of DMBAAPTS.

Assignments	DMBAAPTS	VOCl_2 (DMBAAPTS)	VOBr_2 (DMBAAPTS)	VOI_2 (DMBAAPTS)	$\text{VO}(\text{NO}_3)_2$ (DMBAAPTS)	$\text{VO}(\text{NCS})_2$ (DMBAAPTS)	$\text{VO}(\text{ClO}_4)_2$ (DMBAAPTS) H_2O
$\nu(\text{NH})$	3310 s 3205 s	3310 s 3200 s	3310 s 3200 s	3312 s 3208 s	3310 s 3207 s	3315 s 3205 s	3312 s 3208 s
$\nu(\text{C}=\text{N})$	1608 vs	1555 s	1552 s	1550 s	1560 s	1562 s	1560 s
$\nu(\text{C}=\text{S})+$ $\nu(\text{C}=\text{N})$ $+\nu(\text{C}-\text{N})$	1300 s 1260 vs	1340 s 1265 s	1350 m 1272 s	1345 m 1275 m	1350 m 1270 m	1348 m 1272 m	1335 m 1278 m
$\delta(\text{NCS})$ +CS bending	1132 s 1090 m	1150 m 1122 m	1162 m 1125 m	1158 m 1127 m	1165 m 1125 m	1160 m 1122 m	1152 m 1125 m
$\nu(\text{N}-\text{N})$	1060 m	1075 m	1072 m	1070 m	1078 m	1070 m	1075 m
$\nu(\text{V}=\text{O})$ oxocation	—	980 m	970 m	965 m	972 m	965 m	970 m
$\nu(\text{C}-\text{S})$	840 m 770 s	805 m 720 m	820 m 722 m	810 m 725 m	815 m 722 m	810 m 717 m	812 m 730 m
$\nu(\text{V}-\text{N})$ / $\nu(\text{V}-\text{S})$	—	432 m 328 m	430 m 325 m	432 m 327 m	438 m 330 m	430 m 330 m	438 m 335 m

In all the vanadyl(IV) perchlorato complexes of EBAAPTS and DMBAAPTS, the stretching frequencies above 3400 cm^{-1} region are attributed to $\nu(\text{OH})$. In present complexes of $\text{VO}(\text{ClO}_4)_2(\text{L})\text{H}_2\text{O}$ (L = EBAAPTS or DMBAAPTS), the hydroxyl frequency appears at then same region as in the free ligands, clearly suggesting that the $-\text{OH}$ group is not taking part in the coordination. In the far-infrared region some new bands appearing in the $445\text{-}325\text{ cm}^{-1}$ region are tentatively assigned to $\nu(\text{V-N})$ and $\nu(\text{V-S})$ mode [27, 28]. The presence of coordinated water molecule was suggested by the broad absorption centered around 3450 cm^{-1} in the infrared spectra. Bands at ~ 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water.

According to two reviews of Selbin [29, 30] the $(\text{V}=\text{O})$ stretching frequency is simply too sensitive to other molecular changes to be of much value for such studies. The stretching frequency in present $\text{VO}(\text{IV})$ complexes appeared in $980\text{-}960\text{ cm}^{-1}$ region. The frequencies fall in the reported region which indicates the presence of monomer $\text{V}=\text{O}$ entity in these complexes. Infrared spectroscopy is widely used in the characterization of anions in several compounds. In both perchlorato complexes the presence of the ν_3 ($\sim 1085\text{ cm}^{-1}$) and ν_4 ($\sim 622\text{ cm}^{-1}$) bands indicate that the T_d symmetry of ClO_4^- is maintained in both the complexes which suggests the presence of ClO_4^- outside the coordination sphere of the complexes [31, 32].

The infrared absorption frequencies of both thiocyanate complexes due to C-N stretch (ν_1), C-S stretch (ν_2) and (N-C-S) bending (ν_3) are identified at 2070 , 845 and 472 cm^{-1} respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions [33]. In the spectra of the oxovanadium(II) nitrate complexes, the presence of ν_3 band of ionic nitrate (D_{3h}) occurrence at $\sim 1360\text{ cm}^{-1}$ and occurrence of two strong absorption bands at 1515 and 1300 cm^{-1} attributed to ν_4 and ν_1 modes of vibrations respectively suggest the presence of one coordinated nitrate group [34, 35]. By applying Levers' separation method [36], a separation of 15 cm^{-1} in combination bands ($\nu_1 + \nu_4$) concludes the monodentate nitrate coordination. Other bands appeared at $\sim 1030\text{ cm}^{-1}$ (ν_2), 820 cm^{-1} (ν_6) and 738 cm^{-1} (ν_3/ν_5) due to nitrate group.

Table 4Electronic spectral data (cm^{-1}) of $\text{VO}(\text{IV})$ complexes of thiosemicarbazones.

Complex	Band-I $d_{xy} \rightarrow d_{xz}, d_{yz}$	Band-II $d_{xy} \rightarrow d_{x^2-y^2}$	Band-III $d_{xy} \rightarrow d_{z^2}$
VOCl_2 (EBAAPTS)	13500	15900	22800
VOBr_2 (EBAAPTS)	13000	15600	22600
VOI_2 (EBAAPTS)	12900	15300	—
$\text{VO}(\text{NO}_3)_2$ (EBAAPTS)	12600	15400	21700
$\text{VO}(\text{NCS})_2$ (EBAAPTS)	13300	16000	22000
$\text{VO}(\text{ClO}_4)_2$ (EBAAPTS) H_2O	13400	16100	22500
VOCl_2 (DMBAAPTS)	13000	15900	22000
VOBr_2 (DMBAAPTS)	12800	15200	21700
VOI_2 (DMBAAPTS)	13000	15000	22000
$\text{VO}(\text{NO}_3)_2$ (DMBAAPTS)	12800	15400	22300
$\text{VO}(\text{NCS})_2$ (DMBAAPTS)	13100	15900	—
$\text{VO}(\text{ClO}_4)_2$ (DMBAAPTS) H_2O	13500	15700	22500

3.2. Electronic spectra

In these complexes, the electronic spectra show three low intensity absorption bands in the spectral region 12600-23000 cm^{-1} as shown in Table 4. These are often called d-d or ligand field bands, but for convenience, Selbin [29, 30] refers to these as band-I (up to 16000 cm^{-1}), band-II (between 14500-19000 cm^{-1}) and band-III (between 21000-30000 cm^{-1}) (Table 4).

In present studies the VO(IV) complexes of EBAAPTS and DMBAAPTS are considered to have penta-coordinated environment [29, 30]. The main features of the electronic spectra of the complexes are in agreement with those reported for other similar complexes [34]. In some complexes third ligand field band is obscured charge-transfer bands. According to the Ballhausen and Gray (B.G. Scheme) [35], the assignments of these bands are as band – I to the electron transition $b_2 \rightarrow e_\pi^*$ (or ${}^2B_2 \rightarrow {}^2E_1$), band-II to $b_2 \rightarrow b_1^*$ (or ${}^2B_2 \rightarrow {}^2B_1$) and band-III to $b_2 \rightarrow a_1^*$ (or ${}^2B_2 \rightarrow {}^2A_1$). All other high-energy bands are assumed to be charged transfer in origin. According to Von-Quickenborne and McGlynn [36] the first band, which is centered near 13000 cm^{-1} has been assigned to an unresolved band resulting from $d_{xy} \rightarrow d_{yz}$, d_{xz} (${}^2B_2 \rightarrow {}^2E_1$) transition. The second band is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ (${}^2B_2 \rightarrow {}^2B_1$) and the third band may either be assigned to the transition $d_{xy} \rightarrow d_{z^2}$ (${}^2B_2 \rightarrow {}^2A_1$) or believed to arise from energy charge – transfer.

3.3. Thermal studies

The careful analysis of pyrolysis curves (Table 5) of VOX_2 (EBAAPTS) ($X=\text{Cl}^-$, NO_3^- or NCS^-) suggests that these complexes do not possess water molecule either in or out of the coordination sphere. The pyrolysis curves behave similarly and show that the decomposition of the complexes started at 240 °C and was completed at ~ 460 °C. The break in curves at ~ 310 °C indicate that at this stage 0.5 mole of EBAAPTS had been lost while at ~ 460°C, the loss is corresponding to complete loss of EBAAPTS. The oxide V_2O_5 is formed at around 650-700 °C and there often no sensible change in weight observed [37, 38]. In brief, the thermal decomposition equation is as:

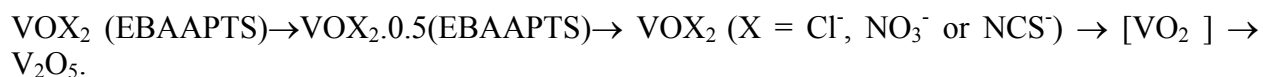


Table 5

Thermoanalytical results of VO(IV) complexes of EBAAPTS.

Complex	Sample wt. (mg)	Residual wt. (mg)	Mass loss (%)						Residual (%)	
			90-145 °C		240-310 °C		370-460 °C		~700 °C	
			Theor ^a	Exp	Theor ^b	Exp	Theor ^c	Exp	Theor ^d	Exp
VOCl_2 (EBAAPTS)	18.10	3.14	–	–	36.98	36.76	73.96	73.26	17.16	17.36
$\text{VO}(\text{NO}_3)_2$ (EBAAPTS)	22.60	3.57	–	–	33.62	33.48	67.23	66.84	15.68	15.82
$\text{VO}(\text{NCS})_2$ (EBAAPTS)	24.80	3.96	–	–	34.08	33.86	68.17	67.86	15.82	15.98
$\text{VO}(\text{ClO}_4)_2$ (EBAAPTS) H_2O	26.80	3.67	2.66	2.70	31.65	31.45	60.65	59.98	13.46	13.71

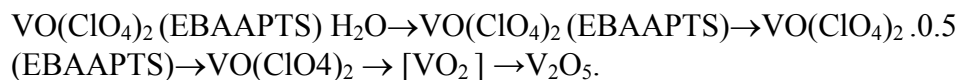
^a Calculated for loss of H_2O mole.

^b Calculated for loss 0.5 mole of EBAAPTS

^c Calculated for total loss of EBAAPTS

^d Calculated as V₂O₅.

The analysis of the thermogravimetric curve of [VO(EBAAPTS)H₂O](ClO₄)₂ indicates the presence of one mole of water inside the coordination sphere. The weight loss in 90-145 °C range is 2.70%, which is corresponding to loss of one water molecule. The decomposition scheme of these complexes is shown by the following thermal equation:



3.4. Biological properties

The antimicrobial screening data on *E. coli* and *K. aerogenus* species are presented in Table 6. The data presented in Table 6, shows that the VO(IV) complexes exhibit antimicrobial properties and it is important to note that their activity is enhanced as compared to the parent ligand.

Table 6

Antibacterial screening data of VO(IV) complexes of thiosemicarbazones.

Compound	Diameter of inhibition zone (mm)(conc.in ppm)			
	<i>E. coli</i>		<i>K. aerogenus</i>	
	500	1000	500	1000
EBAAPTS	7	9	6	8
VOCl ₂ (EBAAPTS)	8	10	7	10
VOBr ₂ (EBAAPTS)	9	10	8	10
VO(NO ₃) ₂ (EBAAPTS)	9	11	8	11
VO(NCS) ₂ (EBAAPTS)	10	11	9	11
DMBAAPTS	9	12	8	10
VOCl ₂ (DMBAAPTS)	10	13	9	11
VOBr ₂ (DMBAAPTS)	11	13	10	12
VO(NO ₃) ₂ (DMBAAPTS)	12	14	11	12
VO(NCS) ₂ (DMBAAPTS)	12	14	12	13
Streptomycin	16	18	16	18

The antifungal activity of VO(IV) complexes of EBAAPTS and DMBAAPTS was evaluated against *Fusarium oxysporum* and *Macrophormina phaseolina* by the agar plate techniques. Solutions of the metal-complexes in different concentrations in DMF were then mixed with the medium. The linear growth of the fungus was recorded by measuring the diameter of colony after 96 hr and the percentage inhibition was calculated as 100(C-T) / C, where C and T are the diameters of the fungus colony in the control and test plates respectively (Table 7).

3.5. Stereochemistry

X-ray diffraction and e.s.r. studies [39] of five – coordinated VO(acac)₂ [40] and VO (Ox)²⁻ show that they have tetragonal pyramidal structure. By close analogy of the electronic spectra of most of the other oxovanadium(IV) complexes [41,42], with these thiosemicarbazones. It is

concluded that the present complexes are also penta-coordinated and may have tetragonal pyramidal structure (Fig. 2a and b).

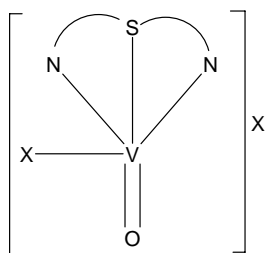


Fig. 2a. Proposed structure of $\text{VOX}_2(\text{L})$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- , or NCS^- and $\text{L} = \text{EBAAPTS}$ or DMBAAPTS).

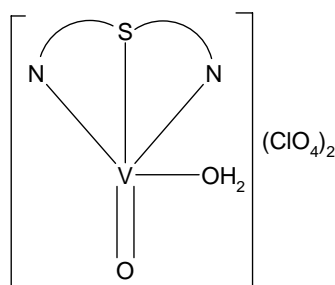


Fig. 2b. Proposed structure of $\text{VO}(\text{ClO}_4)_2\text{L}$ ($\text{L} = \text{EBAAPTS}$ or DMBAAPT).

Table 7

Fungicidal screening data of VO(IV) complexes of thiosemicarbazones.

Compound	Percent inhibition after 96 h (conc. in ppm)					
	<i>Fusarium oxysporium</i>			<i>Macrophonina phaseolina</i>		
	50	100	200	50	100	200
EBAAPTS	40	45	50	40	46	54
$\text{VOCl}_2(\text{EBAAPTS})$	44	52	58	43	49	58
$\text{VOBr}_2(\text{EBAAPTS})$	44	50	57	44	50	58
$\text{VO}(\text{NO}_3)_2(\text{EBAAPTS})$	45	53	56	45	54	57
$\text{VO}(\text{NCS})_2(\text{EBAAPTS})$	48	54	58	47	55	59
DMBAAPTS	44	48	55	47	48	53
$\text{VOCl}_2(\text{DMBAAPTS})$	47	54	59	49	51	55
$\text{VOBr}_2(\text{DMBAAPTS})$	47	55	58	50	52	56
$\text{VO}(\text{NO}_3)_2(\text{DMBAAPTS})$	47	50	57	49	53	56
$\text{VO}(\text{NCS})_2(\text{DMBAAPTS})$	49	53	60	50	55	59
Bavistin	84	100	100	80	99	100

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