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Synthesis, Spectral and Thermal Properties of Some Penta-Coordinated Complexes of Oxovanadium(IV) Derived from Thiosemicarbazones of 4-Aminoantipyrine

Ram K. AGARWAL[1*], Surendra PRASAD[1], Neetu GAHLOT[2]
*[*1] Department of Chemistry, School of Pure and Applied Sciences, The University of the South Pacific, Post Box 1168 Suva-FIJI ISLANDS*
e-mail: agarwal_r@usp.ac.fj, ram_agarwal54@yahoo.com
[2] Department of Chemistry, Lajpat Rai Post Graduate College, Sahibabad-201 005 (Ghaziabad)-INDIA

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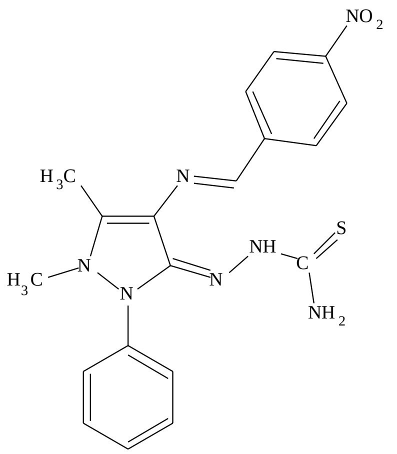
The paper reports the synthesis of crystalline oxovanadium(IV), VO^{2+}, complexes of thiosemicarbazones, i.e. 4[N-(4′-nitrobenzalidene)amino]antipyrine thiosemicarbazone (4′-NO_2BAAPTS) and 4[N-(furan-2'-aldimine)amino]antipyrine thiosemicarbazone (FFAAPTS) with general composition VOX_2L (X = Cl, Br, I, NO_3 or NCS) and $VO(ClO_4)_2(L)H_2O$ (L = 4′-NO_2BAAPTS or FFAAPTS). All the complexes were characterized by elemental analyses, molar mass, molar conductance, magnetic susceptibility, infrared and electronic spectra. In all the 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.

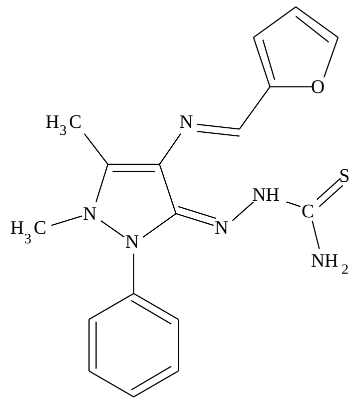
Introduction

Although there are nearly 60 oxometal entities known with transition metals of the type MO_x^{n+}, only 2, UO_2^{2+} and VO^{2+}, have been prepared in a large number of varieties of stable complexes[1−4]. Oxovanadium(IV) forms stable complexes with 4-aminoantipyrine[3]. A careful literature survey[4−7] reveals that only one report has been published on oxovanadium(IV) complexes of thiosemicarbazones derived from 4-aminoantipyrine[7]. Thus, it was worthwhile to report the synthesis, spectral and thermal properties of crystalline VO^{2+} complexes of 4[N-(4′-nitrobenzalidene)amino]antipyrine thiosemicarbazone (4′-NO_2BAAPTS) **(I)** and 4[N-(furan-2′-aldimine)amino]antipyrine thiosemicarbazone (FFAPTS) **(II)**. The structures of the ligands are shown below:

*Corresponding author



4'-NO_2BAAPTS **(I)**



FFAPTS **(II)**

Experimental

Oxovanadium(IV) chloride and bromide were prepared by treating vanadium pentoxide with concentrated hydrochloric acid and hydrobromic acid respectively in the presence of a few drops of ethanol[8]. Oxovanadium(IV) perchlorate was prepared by the method of Sathyanarayana and Patel[9]. Oxovanadium(IV) iodide in solution was prepared by treating an alcoholic solution of $VOCl_2$ with KI in a 1:2 molar ratio and the reaction mixture was stirred on a magnetic stirrer for about 30min. The precipitated KCl was filtered off and the filtrate containing VOI_2 was used for the preparation of the complexes in the present report. Oxovanadium(IV) thiocyanate solution was prepared by treating an aqueous solution of oxovanadium(IV) perchlorate with potassium thiocyanate. The clear blue filtrate obtained after removal of the solid was concentrated by passing through dry air when syrupy green solution was obtained as oxovanadium(IV) thiocyanate. Oxovanadium(IV) nitrate was prepared by treating solution of oxovanadium(IV) chloride with silver nitrate solution. Both the ligands 4′-NO_2BAAPTS and FFAAPTS were synthesized in the laboratory by a known method[10]. The solvents were obtained from standard sources such as BDH or E. Merck.

Synthesis of the complexes

All the complexes of oxovanadium(IV) were isolated by the following general methods:

i) A hot ethanolic (20 mL) solution of the respective ligand (2 mmol) and a hot aqueous ethanol (1:1, v/v) solution of the corresponding metal salt (2 mmol) were mixed together. The content was boiled under reflux on a water bath for ∼1 h. On cooling the reaction mixture to room temperature, a blue to green complex was precipitated out and then filtered, washed with ethanol and dried under vacuum over P_4O_{10} (yield 60% -70%).

ii) In another method, a hot ethanolic solution (20 mL) of the ligand (2 mmol) and a hot aqueous ethanol (20 mL, 1:1, v/v, EtOH/H_2O) solution of the corresponding metal salt (2 mmol) were mixed together and the contents were refluxed on a water bath for ∼2 h. The solution was then concentrated to half of its original volume. On cooling the contents, a blue or green complex was precipitated out and then filtered, washed with ethanol and finally with dry ether and kept over P_4O_{10}(yield ∼ 66% -70%).

Analytical techniques

IR spectra (in KBr pellets) were recorded on a Perkin-Elmer 5998 (4000-200 cm^{-1}) spectrophotometer and all other physico-chemical measurements were performed as reported earlier[3,5]and vanadium was estimated as V_2O_5.

Results and Discussion

The reaction of VO^{2+} salts with 4′-NO_2BAAPTS and FFAAPTS gave complexes of the general composition VOX_2L (X = Cl, Br, I, NO_3 or NCS) or $VO(ClO_4)_2(L)H_2O$ (L = 4′-NO_2BAAPTS or FFAAPTS). The analytical data of these complexes are presented in Table 1. All the complexes are quite stable and could be stored for months without any appreciable change. These complexes are generally soluble in common organic solvents. The molar conductance values (Table 1) of VO^{2+} complexes indicate that except for oxovanadium(IV) perchlorato complexes all complexes of VO^{2+} behave like 1:1 electrolytes; while perchlorato complexes are 1:2 electrolytes. The molecular weights determined by the cryoscopic method in nitrobenzene are given in Table 1. The results are in good agreement with the conductance data. The magnetic moments of these complexes were measured at ∼37 °C and found to be in 1.73-1.89 B.M. (Table 1). These values are well within the range observed for the VO(IV) complexes and correspond to one unpaired spin per vanadium atom, demonstrating the tetravalency of vanadium in the complexes[11−13].

Infrared spectra

A study and comparison of the infrared spectra of free ligands (4′-NO_2BAAPTS and FFAAPTS) and their VO^{2+} complexes (Tables 2 and 3) imply that both ligands behave as neutral tridentate and the metal is coordinated through N and N of 2 azomethine groups and of S of a thioketo group.

The strong bands observed at 3440-3270 cm^{-1} in both ligands were due to ν(N–H) vibrations. The practically absent effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorptions at ∼1600 cm^{-1} in free ligands can be attributed to (C=N) stretching vibrations of imine nitrogen, which is in agreement with the observations of previous workers[14,15]. On complexation these frequencies were observed to be shifted to a lower wave number (Tables 2 and 3). These observations suggest the involvement of the unsaturated nitrogen atoms of the 2 azomethine groups in bonding with the metal ions.

In substituted thioureas, the (C=S) stretching vibrations contributed much with some other vibrations as (C–N) stretching and bending as well as (N–C–S) bending modes[16]. Following the observations of Swaminathan and Irving[17] and some other researchers[18], in the spectra of the present ligands, the bands observed at 1300-1185 cm^{-1}, 1120-1095 cm^{-1} and 840-730 cm^{-1} are assigned to [ν(C=S) + ν(C=N) + ν(C–N)], [δ(N–C–S) + δ(C=S)] and (C=S) stretchings, respectively. Coordination of sulfur with the metal ion would result in the displacement of electrons towards the latter, resulting in the weakening of the (C=S) bond. Hence, on complexation (C=S) stretching vibrations should decrease and those of (C–N) should increase[18]. In all the present complexes, frequencies in the range 1315-1185 cm^{-1} increase by nearly 50-60 cm^{-1}. Similarly, bending modes of (N–C–S) and (C=S) also increase but in lesser amounts.

Table 1. Analytical, conductivity, molecular weight and magnetic moment data of VO^{2+}complexes of 4′-NO_2BAAPTS and FFAAPTS.

Complex	Yield (%)	Analysis: Found (Calcd) %				m.w. Found (Calcd) %	Ω m (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff}(B.M.)
		V	N	S	Anion			
$VOCl_2$(4′-NO_2BAAPTS)	75	9.29 (9.32)	17.87 (17.91)	5.81 (5.85)	12.86 (12.97)	271 (547)	24.1	1.82
$VOBr_2$(4′-NO_2BAAPTS)	70	7.97 (8.01)	15.34 (15.4)	4.98 (5.03)	25.06 (25.15)	317 (636)	23.6	1.89
VOI_2(4′-NO_2BAAPTS)	68	6.9 (6.98)	13.37 (13.42)	4.34 (4.38)	34.69 (34.79)	358 (730)	24.9	1.8
$VO(NO_3)_2$(4′-NO_2BAAPTS)	70	8.43 (8.5)	20.89 (21)	4.29 (5.33)	--	297 (600)	23.9	1.79
$VO(NCS)_2$(4′-NO_2BAAPTS)	72	19.09 (19.17)	22.59 (22.66)	17.19 (17.26)	20.73 (20.86)	274 (556)	24.7	1.73
$VO(ClO_4)_2$(4′-NO_2BAAPTS)H_2O	65	7.3 (7.35)	14.07 (14.14)	4.57 (4.61)	28.6 (28.71)	237 (693)	52.3	1.75
$VOCl_2$(FFAAPTS)	73	10.46 (10.36)	17.00 (17.07)	6.43 (6.50)	14.29 (14.43)	251 (492)	24.9	1.76
$VOBr_2$(FFAAPTS)	70	8.83 (8.77)	14.39 (14.45)	5.44 (5.5)	27.46 (227.53)	293 (581)	24.3	1.82
VOI_2(FFAAPTS)	65	7.61 (7.55)	12.36 (12.44)	4.7 (4.74)	37.51 (37.62)	340 (675)	25.6	1.79
$VO(NO_3)_2$(FFAAPTS)	70	9.4 (9.35)	20.43 (20.55)	5.83 (5.87)	--	275 (545)	26.7	1.83
$VO(NCS)_2$(FFAAPTS)	65	9.42 (9.49)	20.75 (20.85)	17.69 (17.87)	21.52 (21.6)	270 (537)	24.9	1.75
$VO(ClO_4)_2$(FFAAPTS)H_2O	60	7.96 (7.99)	13.08 (13.16)	4.98 (5.01)	31.02 (31.19)	210 (638)	51.2	1.80

Table 2. Infrared absorption frequencies (cm^{-1}) of VO^{2+} complexes of 4′-NO_2BAAPTS.

Assignments	4′-NO_2BAAPTS	$VOCl_2$ 4′-NO_2BAAPTS	$VOBr_2$ 4′-NO_2BAAPTS	VOI_2 4′-NO_2BAAPTS	$VO(NO_3)_2$ 4′-NO_2BAAPTS	$VO(NCS)_2$ 4′-NO_2BAAPTS	$VO(ClO_4)_2$ 4′-NO_2(BAAPTS)H_2O
v(N–H)	3355 s 3330 m	3350 m 3330 m	3362 m 3337 w	3360 m 3332 w	3360 m 3330 m	3362 m 3332 m	3360 m 3332 w
v(C=N)	1600 vs	1565 m	1570 m	1568 m	1570 m	1565 m	1560 m
v(C=S) + v(C=N) + v(C–N)	1310 m 1290 m	1370 m 1335 m	1365 m 1340 m	1372 m 1335 m	1370 m 1340 m	1372 m 1342 m	1370 m 1342 m
δ (N–C–S) + C–S bending	1115 m 1095 w	1170 m 1130 m	1165 m 1130 m	1170 m 1135 m	1160 m 1140 m	1165 m 1125 m	1160 m 1130 m
v(N–N)	1032 m	1062 m	1065 m	1065 m	1068 m	1065 m	1060 m
v(C=S)	832 s 730 m	780 m 710 m	770 s 705 m	775 m 710 m	775 m 715 m	775 m 720 m	770 m 715 m
v(V–N)/ v(V–S)	-	340 m 310 w	352 m 320 w	342 m 315 w	360 m 312 w	345 m 320 w	348 m 315 w
v(V–Cl)	-	350 w	-	-	-	-	-

Table 3. Infrared absorption frequencies (cm^{-1}) of VO^{2+} complexes of FFAAPTS.

Assignments	FFAAPTS	$VOCl_2$ (FFAAPTS)	$VOBr_2$ (FFAAPTS)	VOI_2 (FFAAPTS)	$VO(NO_3)_2$ (FFAAPTS)	$VO(NCS)_2$ (FFAAPTS)	$VO(ClO_4)_2$ (FFAAPTS)H_2O
ν (N–H)	3440 s	3442 m	3440 m	3440 m	3440 m	3442 m	3440 m
	3280 s	3282 m	3285 m	3282 m	3280 m	3280 m	3282 m
ν (C=N)	1600 vs	1560 s	1565 s	1562 s	1560 s	1565 s	1562 s
ν (C–S) + ν (C=N) + ν (C–N)	1315 s 1185 m	1370 s 1205 m	1372 s 1205 m	1370 s 1210 m	1370 s 1215 m	1372 s 1218 m	1365 s 1210 m
δ (N–C–S) + C–S bending	1122 m 1095 m	1160 m 1130 m	1165 m 1130 m	1162 m 1135 m	1160 m 1135 m	1165 m 1130 m	1165 m 1132 m
ν (N–N)	1040 m	1052 m	1050 m	1055 m	1050 m	1058 m	1052 m
ν (C=S)	840 s 820 m 780 s	810 s 792 m	805 s 782 m	810 s 790 m	808 s 785 m	812 s 775 m	812 m 780 m
ν (N–N)/	—	350 m	342 m	352 m	355 m	345 m	345 m
ν (V–S)		315 w	320 w	322 w	318 w	325 w	320 w
ν (V–Cl)	—	352 w	—	—	—	—	—

On the other hand, on complexation the frequencies at 840-730 cm^{-1} are shifted to lower wave numbers and the intensity of the bands is also reduced. All these peculiar changes on complexation confidently preclude any unambiguous ascertaining of the (V–S) band. The possibility of thion-thiol tautomerism (H–N–C=S) $\rightleftharpoons$ (C=N–SH) in these ligands has been ruled out for no bands around 2700-2500 cm^{-1},and the characteristics of the thiol group are displayed in the IR absorption[19,20].

The far IR spectral bands in both ligands are practically unchanged in the complexes but show some new bands with medium to weak intensity in 360-310 cm^{-1} region are tentatively assigned to ν(V–N)/ν(V–S) in accordance with various other reports[21,22]. Thus, the infrared spectral studies suggest the tridentate (N,N,S) nature, by pointing out the sites of possible donor atoms. In all the complexes of oxovanadium(IV) under discussion, the (V=O) stretching frequency occurs in the 980-960 cm^{-1} region. These values are within the range observed for monomeric VO^{2+} complexes[1−3,23].

In perchlorato complexes, the presence of coordinated water was suggested by the very broad absorption centered around 3450 cm^{-1}. Bands at ~930 and 770 cm^{-1} may be attributed to the rocking and wagging modes of the coordinated water[24]. The presence of numerous bands in the spectra of thiosemicarbazone complexes of VO^{2+} complicates the identification of the nature of the coordination of nitrate, perchlorate and thiocyanate groups. However, a close comparison of the spectra makes some inferences possible.

In the nitrate complexes, the absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of 2 strong bands at ~1510 and 1300 cm^{-1} due to the split ν_3 mode in the lower symmetry indicate a coordinated nitrato group[25,26]. Distinction between monodentate and bidentate nitrate is usually difficult. However, by applying Lever's separation method[27], a separation (~20-25 cm^{-1}) of the combination bands ($\nu_1 + \nu_4$) indicates monodentate nitrate coordination. Other bands appeared at ~1030 (ν_2), 805 (ν_6) and 730 cm^{-1} (ν_3/ν_5) due to nitrato groups.

In the perchlorato complexes, the ν_3 and ν_4 bands of the perchlorato group appear at ~1090 and 625 cm^{-1}, respectively. This indicates that the tetrahedral symmetry has not been disturbed in the complexes and all the perchlorato ions are present outside the coordination field[3,28]. In thiocyanato complexes, the 3 fundamental absorptions ν(C–N) (ν_1), ν(C–S)(ν_3) and δ(N–C–S)(ν_2) are identified at ~2040, 840 and 470 cm^{-1}, respectively. The frequencies are associated with terminal N-bonded isothiocyanate ions[29].

Electronic spectra

All the oxovanadium(IV) complexes studied here in exhibit 2 electronic bands in the 12,500-17,500 cm^{-1} region. These bands are not well developed. In some complexes, a weak but well developed band at ~23,000 cm^{-1} was also observed (Table 4). The assignment of electronic spectral bands of VO(IV) complexes has been a subject of controversy[30,31]. Ballhausen and Gray (BG scheme)[(32)] have provided a convenient energy level scheme for VO(IV) type complexes. In general, oxovanadium(IV) complexes display 3 low intensity bands in the 12,000-24,000 cm^{-1} range (Table 4). According to the BG scheme, the first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond 30,000 cm^{-1}). Generally band-III is not observed and is thought to be buried beneath the low energy tail of the much more intense charge transfer band but it was observed in the present complexes. Following the ordering of energy levels (BG scheme), the first shoulder, which is centered at about 13,000 cm^{-1}, is assigned to a unresolved band resulting from the $d_{xy} \rightarrow d_{xz} \rightarrow d_{yz}$ ($^2B_2 \rightarrow ^2E$) transition. The second band (in the region 15,300-17,500 cm^{-1}) is attributed to $d_{xy} \rightarrow d_{x2-y2}$ ($^2B_2 \rightarrow ^2B_1$) transitions. The band at about 22,000 cm^{-1} may either be assigned to the $d_{xy} \rightarrow d_{z2}$ ($^2B_2 \rightarrow ^2A_1$) transition or is thought to be a low energy charge transfer band.

Table 4. Electronic spectral data (cm^{-1}) of VO(IV) complexes of 4′-NO_2BAAPTS and FFAAPTS.

Complex	Band-I $d_{xy} \rightarrow d_{xz},d_{yz}$	Band-II $d_{xy} \rightarrow d^2_{x}\text{-}^2_{y}$	Band-III $d_{xy} \rightarrow d^2_z$
$VOCl_2$(4′-NO_2BAAPTS)	13,400	17,200	23,300
$VOBr_2$(4′-NO_2BAAPTS)	13,200	17,300	-
VOI_2(4′-NO_2BAAPTS)	13,300	17,250	23,000
$VO(NO_3)_2$(4′-NO_2BAAPTS)	13,500	17,350	22,000
$VO(NCS)_2$(4′-NO_2BAAPTS)	13,300	17,150	22,500
$VO(ClO_4)_2$(4′-NO_2BAAPTS)H_2O	13,350	17,200	22,000
$VOCl_2$(FFAAPTS)	12,900	15,900	22,200
$VOBr_2$(FFAAPTS)	12,700	15,200	22,500
VOI_2(FFAAPTS)	13,050	15,600	22,300
$VO(NO_3)_2$(FFAAPTS)	13,100	15,500	22,000
$VO(NCS)_2$(FFAAPTS)	12,950	15,700	22,200
$VO(ClO_4)_2$(FFAAPTS)H_2O	12,800	15,750	22,300

Thermal studies

The thermogravimetric analysis of the oxovanadium complexes of FFAAPTS was carried out and the results of these complexes are summarized in Table 5. The thermal data on VOX_2(FFAAPTS) (X = Cl, NO_3 or NCS) clearly indicate that all the complexes are non-hygroscopic in nature, with no water of crystallization. The complexes started to lose mass in open air at ∼230 °C with evaporation of the ligand up to 310 °C corresponding to 0.5 mol of organic ligand. The complete loss of ligand occurred at ∼420 °C. The residues obtained at constant weight (∼640 °C) are very close to those expected for V_2O_5. All the complexes studied decomposed according to the general equation as indicated below.

VOX_2(FFAAPTS) → VOX_2.0.5(FFAAPTS) → VOX_2 → [VO_2] → V_2O_5

(X = Cl, NO_3 or NCS)

The analysis of the thermogravimetric curves of [VO(FFAAPTS)H_2O]$(ClO_4)_2$ indicates the presence of one molecule of water present inside the coordination sphere. The weight loss in the 100-140 °C range is ∼2.62%, which corresponds to one water molecule. The decomposition scheme of this complex is shown by the following thermal equation:

$VO(ClO_4)_2$(FFAAPTS)H_2O → $VO(ClO_4)_2$(FFAAPTS) → $VO(ClO_4)_2$0.5(FFAAPTS) → $VO(ClO_4)_2$ → [VO_2] → V_2O_5

In conclusion, due to steric interactions of the larger ligands, the lower coordination number 5 has been assigned to these complexes. The 5- coordinated thiosemicarbazone complexes of VO^{2+}may have the usual tetragonal pyramidal structure as shown in Figures 1 and 2.

Table 5. Thermoanalytical results obtained for VO(IV) complexes of FFAAPTS.

Complex	Sample wt (mg)	Residual wt (mg)	Mass loss (%)						Residual (%)	
			100-140 °C		230-310 °C		370-420 °C		~640°C	
			Theor[a]	Exp	Theor[b]	Exp	Theor[c]	Exp	Theor[d]	Exp
$VOCl_2$(FFAAPTS)	16.20	2.96	-	-	35.97	36.20	71.95	73.20	18.49	18.28
$VO(NO_3)_2$(FFAAPTS)	14.80	2.43	-	-	32.92	32.92	64.95	65.86	16.69	16.44
$VO(NCS)_2$(FFAAPTS)	13.20	2.20	-	-	33.42	33.42	65.92	66.70	16.94	16.72
$VO(ClO_4)_2$(FFAAPTS)H_2O	12.60	1.77	2.82	2.89	30.56	30.56	58.30	59.08	14.26	14.08

a - Calculated for loss of H_2O mol
b - Calculated for loss of 0.5 mol of FFAAPTS
c - Calculated for total loss of FFAAPTS
d – Calculated as V_2O_5

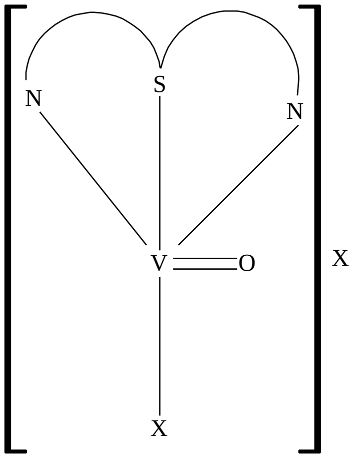


Figure 1. Probable structure of [VO(L)X]X complexes; (X = Cl, Br, NO_3 or NCS and L = 4′-NO_2BAAPTS or FFAAPTS).

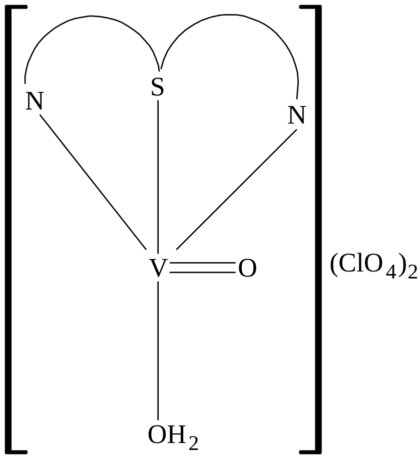


Figure 2. Probable structure of $[VO(L_2)](ClO_4)_2$ complexes; L = 4′-NO_2BAAPTS or FFAAPTS).

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