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Synthesis & Characterization of OxoVanadium(IV) Complexes of 4- [N-Substituted Amino]Antipyrine Morpholino Methyl Thiourea

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Abstract:

New oxovanadium (iv) complexes were synthesized. Schiff 's base of 4-amino antipyrine with different aromatic aldehydes were synthesized which were then condensed with morpholino methyl thiourea to give ligands (L_1-L_4). The ligands were reacted with different oxovanadium (iv) salts to form complexes. The complexes were characterized and their structures established by various physio-chemical techniques viz elemental analysis, conductivity measurement, estimation of anions, IR, magnetic moment molecular weight. On the basis of above observations the complexes may be formulated as [VOLX]X and [VOLX]$(ClO_4)_2$

Keywords: Ligands, Oxovanadium (iv) complexes , Schiff's base , molar conductance

1. Introduction:

The semicarbazone and thiosemicarbazone usually behave as chelating ligand and react with metallic cations giving complexes which have been receiving considerable attention because of their antibacterial(1-2), antifungal(3), antitumor(4), antiviral(5), antimalarial and anti-inflammatory activities (6-8).In the present work we have synthesized oxovanadium complexes of 4-[N- substituted amino] antipyrine morpholino methyl thiourea which have been characterized through various physiochemical techniques.

2. Experimental:

2.1. Materials Used:

All the chemical used were of analytical R grade and procured from spectrochem. All the solvents obtained commercially were distilled before use .

2.2. Synthesis of Metal Salts :

Oxovanadium (iv) chloride and bromide were prepared by treating vanadium pentoxide with concentrated hydrochloric and hydrobromic acids respectively. (9)

Oxovanadium (iv) perchlorate was prepared by literature method .(10)

Oxovanadium (iv) iodide was prepared by treating alcoholic solution of $VOCl_2$ with NH_4I in 1:2 molar ratio and the reaction mixture stirred for about one hour. The precipitated NH_4Cl was removed and the filtrate containing VOI_2 was obtained .

Oxovanadium (iv) thiocyanate was prepared by treating an aqueous solution of oxovanadium (iv) perchlorate with ammonium thiocyanate .

Oxovanadium (iv) nitrate was prepared by treating solution oxovanadium (iv) chloride with silver nitrate solution.

Oxovanadium (iv) oxalate was reported by literature (11)

2.3. Synthesis of Ligand

:

L_1 – N-[(P-Chloro benzalidene)amino] antipyrine morpholino methylthiourea($C_{24}H_{27}ON_6SCl$)

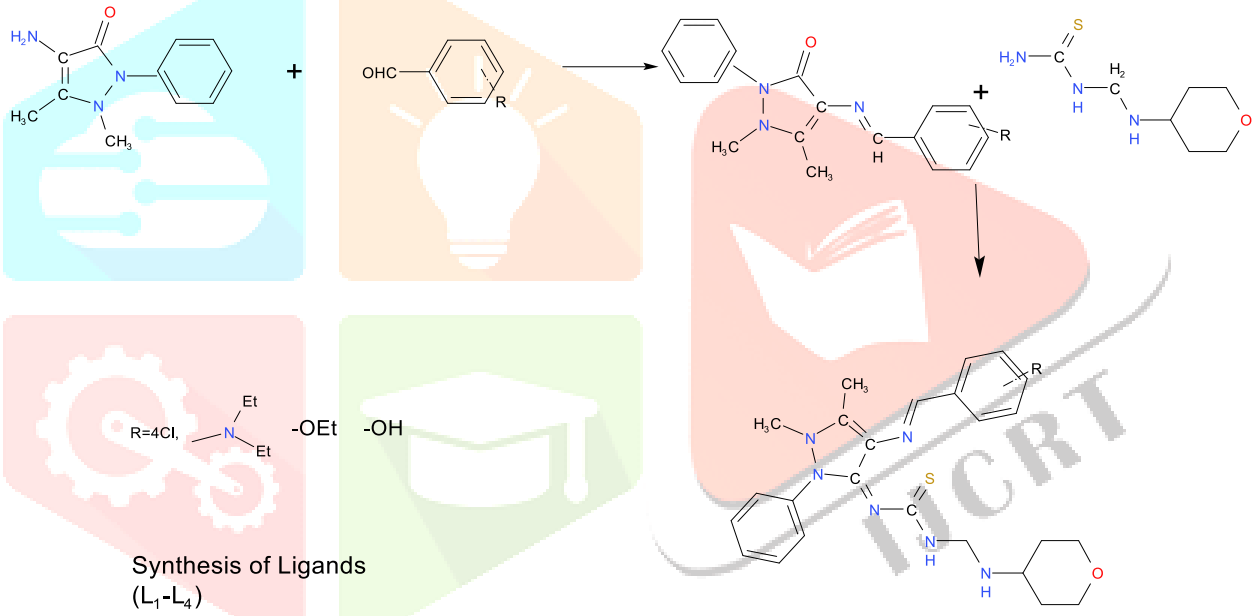
An ethanolic to a solution of 4-amino antipyrine(10mmol,2.03gm) was added to a solution of P-chlorobenzaldehyde(10mmol,1.40gm) in ethanol(10ml).The mixture was refluxed for one hour. The coloured precipitation was obtained by slow evaporation of the solution to give N-[(P-Chlorobenzalidene) amino]antipyrine. This was then condensed with morpholino methyl urea to give N-[(P-Chlorobenzaldene) amino] antipyrine morpholino methylthiourea($C_{24}H_{27}ON_6SCl$). Similarly other ligands were synthesized.

L_2- 4-[N(4-diethyl aminobenzalidene)amino] antipyrine morpholino methylthiourea($C_{28}H_{37}ON_7S$).

L_3- 4-[N-(4-ethoxybenzalidene)amino]antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_2N_6S$)

L_4- 4-[N-(4-hydroxy-3-ethoxybenzalidene) amino]antipyrine morpholino thiourea

($C_{26}H_{32}O_3N_6$ S)



Synthesis of Ligands (L_1-L_4)

2.4. Synthesis of complexes:

The metal chelates were prepared by refluxing the aqueous methanolic solution of metal salts (0.01 mol) and the ligand (0.01 mol each) on a water bath for about 5-6 hours. After completion of reaction, precipitate appeared which were washed successively with alcohol and ether and dried in vacuo over P_4O_{10}.

2.5. Physical Measurements:

C,H,N, were analysed using Perkin- Elmer 240 elemental analyzer. Molar conductance was measured on the systronics conductivity bridge. Infrared spectra of ligand and their complexes have been recorded in KBr pellets on a Perkin-Elmer infracord spectrophotometer. The molar conductance data of all the complexes suggest that the complexes behave as 1:1 electrolytes while the perchlorate complexes are 1:2 electrolytes

and may be formulated as [VOLX]X and $[VOLX](ClO_4)_2$ respectively.

2.6. Magnetic moment:

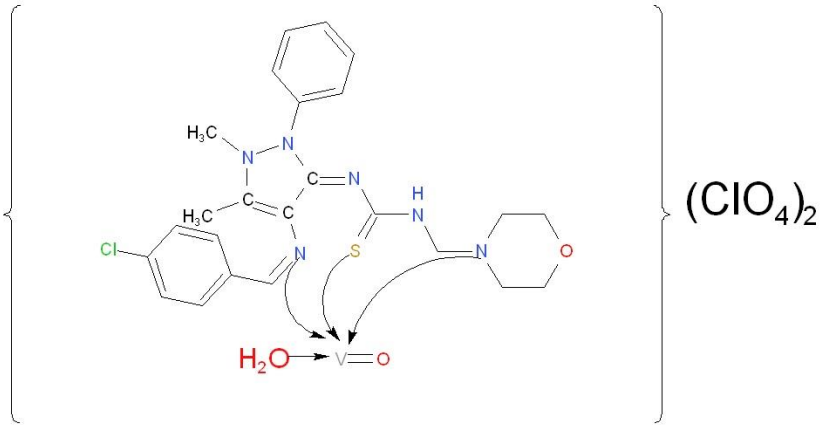
The vanadyl complexes shows magnetic moment value around 1.60-1.85 B.M. which are close to the spin only values expected for $3d^1$ configuration.

2.7. Electronic Spectra:

The vanadyl complexes exhibits three bands in the region 11000-16000 cm^{-1}, 14500-19000 cm^{-1} 21000-30000 cm^{-1} which may be assigned to dxy –> dyz, dzx ($^2B_2$-$^2E_1$) dxy--> dx^2-y^2($^2B_2$-$^2B_1$) and dxy--> dz^2 ($^2B_2$-$^2A_1$) respectively indicating triagonal bipyramidal geometry for all vanadyl complexes.

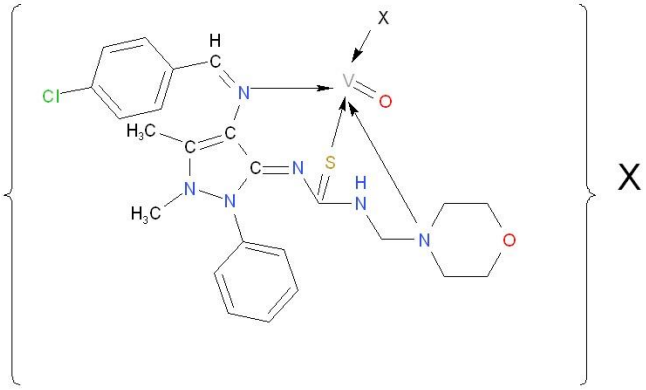
3. Results and Discussion:

The reaction of methanolic solution of ligands (L_1-L_4) with metal salt gave the complex [VOLX]X and [VOLX]$(ClO_4)_2$ as established on the basis of microanalysis, molar conductance value, magnetic studies and IR suggest triagonal bipyramidal geometry.



$[VO(C_{24}H_{27}ON_6SCl)H_2O](ClO_4)_2$

$(C_{24}H_{27}ON_6SCl)$-N-[(p-chloro benzalidene)amino]antipyrine morpholino methyl thiourea



$[VO(C_{24}H_{27}ON_6SCl)X]X$ (X=Cl,Br,I,NCS or NO_3) (C.N.=5)

$(C_{24}H_{27}ON_6SCl)$-N-[(p-chloro benzalidene)amino]antipyrine morpholino methyl thiourea

Probable Structure of Complexes

TABLE 1: Analytical, Conductivity, Molecular weight and Magnetic moment data of VO^{2+} complexes of 4- N[p-(chloro benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{24}H_{27}ON_6SCl$)

S.No	Complexes	Yield (%)	Chemical analysis Found (Calcd.) %					Mol. Wt Found (Calcd.)	ΩM	B.M.
			V	C	H	N	Anion			
1	$VOCl_2(C_{24}H_{27}ON_6SCl)$	75	8.10 (8.21)	46.30 (46.41)	4.10 (4.35)	13.40 (13.53)	5.0 (5.15)	294.0 (620.44)	21.90	1.68
2	$VOBr_2(C_{24}H_{27}ON_6SCl)$	70	7.09 (7.18)	40.59	3.80	11.84	4.51	337 (709.44)	22.86	1.70
3	$VOI_2(C_{24}H_{27}ON_6SCl)$	70	6.20 (6.34)	35.70 (35.84)	3.20 (3.36)	10.32 (10.45)	3.84 (3.98)	396 (803.44)	34.18	1.79
4	$VO(NO_3)_2(C_{24}H_{27}ON_6SCl$	75	7.40 (7.50)	42.60 (42.76)	3.90 (4.00)	16.50 (16.63)	4.6 (4.75)	319 (673.44)	22.70	1.76
5	$VO(NCS)_2(C_{24}H_{27}ON_6SCl$	70	7.50 (7.50)	46.72 (46.88)	3.90 (4.05)	16.70 (16.83)	14.30 (14.32)	314 (665.44)	25.05	1.70
6	$VO(ClO_4)_2(C_{24}H_{27}ON_6SCl$ $.H_2O$	70	6.70 (6.80)	38.32 (38.48)	3.70 (3.87)	11.10 (11.22)	4.15 (4.27)	238 (748.44)	55.05	1.78

TABLE 2: Analytical, Conductivity, Molecular weight and Magnetic moment data of VO^{2+} complexes of 4[N-(4-Diethyl amino benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{28}H_{37}ON_7S$)

S.No	Complexes	Yield (%)	Chemical analysis Found (Calcd.) %					Mol. Wt Found (Calcd.)	ΩM	B.M.
			V	C	H	N	S			
1	$VOCl_2(C_{28}H_{37}ON_7S)$	70	8.0 (8.12)	53.40 (53.59)	5.80 (5.90)	15.42 (15.63)	5.0 (5.10)	301 (626.94)	23.10	1.78
2	$VOBr_2(C_{28}H_{37}ON_7S)$	70	7.0 (7.11)	46.80 (46.93)	5.0 (5.16)	13.52 (13.68)	4.3 (4.46)	342 (715.94)	24.90	1.75
3	$VOI_2(C_{28}H_{37}ON_7S)$	65	6.18 (6.28)	41.30 (41.48)	5.10 (5.16)	11.90 (12.09)	3.80 (3.95)	394 (809.94)	23.72	1.80
4	$VO(NO_3)_2(C_{28}H_{37}ON_7S)$	75	7.32 (7.49)	49.30 (49.41)	5.32 (5.44)	18.40 (18.53)	4.60 (4.70)	319 (676.94)	26.50	1.77
5	$VO(NCS)_2(C_{28}H_{37}ON_7S)$	70	7.43 (7.58)	53.40 (53.57)	5.40 (5.50)	18.60 (18.75)	14.18 (14.28)	264 (671.94)	24.10	1.77
6	$VO(ClO_4)_2(C_{28}H_{37}ON_7S)$ $.H_2O$	70	6.40 (6.59)	43.32 (43.47)	4.90 (5.04)	12.50 (12.67)	4.0 (4.14)	248 (772.94)	57.70	1.76

TABLE 3: Analytical, Conductivity, Molecular weight and Magnetic moment data of VO^{2+} complexes of N-[(4-hydroxy-3-ethoxy benzalidene)amino]antipyrine morpholino thiourea ($C_{26}H_{32}O_2N_6S$)

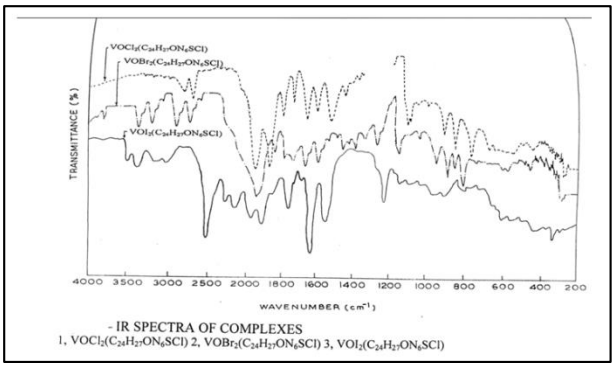
S.No	Complexes	Yield (%)	Chemical analysis Found (Calcd.) %					Mol. Wt Found (Calcd.)	ΩM	B.M.
			V	C	H	N	Anion			
1	$VOCl_2(C_{26}H_{32}O_2N_6S)$	70	7.60 (8.0)	49.40 (49.52)	4.90 (5.07)	13.20 (13.33)	4.90 (5.07)	293 (629.94)	21.82	1.74
2	$VOBr_2(C_{26}H_{32}O_2N_6S)$	72	6.90 (7.08)	43.39 (43.20)	4.30 (4.45)	11.50 (11.68)	4.3 (4.45)	343 (718.94)	25.30	1.72
3	$VOI_2(C_{26}H_{32}O_2N_6S)$	75	6.10 (6.26)	38.20 (38.37)	3.80 (3.93)	10.20 (10.33)	3.8 (3.93)	280 (812.94)	33.60	1.76
4	$VO(NO_3)_2(C_{26}H_{32}O_2N_6S)$	80	7.30 (7.45)	45.50 (45.68)	4.5 (4.68)	16.25 (16.39)	4.53 (4.68)	331 (682.94)	25.12	1.78
5	$VO(NCS)_2(C_{26}H_{32}O_2N_6S)$	78	7.45 (7.54)	49.62 (49.78)	4.63 (4.74)	16.42 (16.59)	14.10 (14.22)	327 (674.94)	28.50	1.70
6	$VO(ClO_4)_2(C_{26}H_{32}O_2N_6S)$ $.H_2O$	70	6.40 (6.56)	40.10 (40.20)	4.22 (4.38)	10.70 (10.82)	4 (4.12)	248 (775.94)	55.20	1.78

TABLE 4: Analytical, Conductivity, Molecular weight and Magnetic moment data of VO^{2+} complexes of N-[(4-ethoxy benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{24}H_{32}O_3N_6S$)

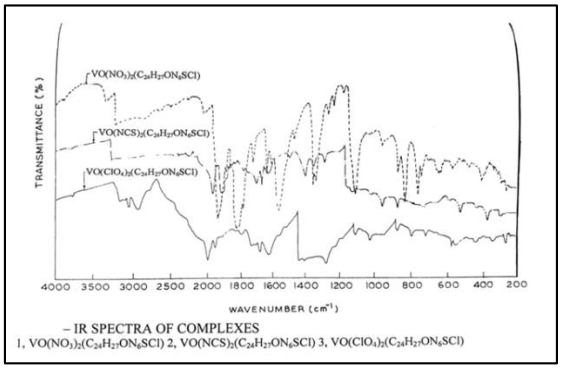
S.No	Complexes	Yield (%)	Chemical analysis Found (Calcd.) %					Mol. Wt Found (Calcd.)	ΩM	B.M.
			V	C	H	N	Anion			
1	$VOCl_2(C_{24}H_{32}O_3N_6S)$	70	7.70 (7.88)	48.15 (48.30)	4.82 (4.95)	12.85 (13.0)	4.84 (4.95)	310 (645.94)	21.70	1.78
2	$VOBr_2(C_{24}H_{32}O_3N_6S)$	72	6.80 (6.93)	42.30 (42.45)	4.20 (4.35)	11.30 (11.42)	4.20 (4.35)	349 (734.94)	22.64	1.75
3	$VOI_2(C_{24}H_{32}O_3N_6S)$	70	6.0 (6.14)	37.50 (37.63)	3.70 (3.86)	10.0 (10.13)	3.70 (3.86)	537 (828.94)	35.10	1.68
4	$VO(NO_3)_2(C_{24}H_{32}O_3N_6S)$	75	7.13 (7.28)	44.50 (44.63)	4.40 (4.57)	15.90 (16.02)	4.43 (4.57)	328 (698.94)	30.05	1.72
5	$VO(NCS)_2(C_{24}H_{32}O_3N_6S)$	80	7.20 (7.32)	48.50 (48.62)	4.53 (4.69)	16.10 (16.20)	13.75 (13.89)	323 (690.94)	25.70	1.76
6	$VO(ClO_4)_2(C_{24}H_{32}O_3N_6S)$ $.H_2O$	70	6.43 (6.58)	40.20 (40.31)	4.25 (4.39)	10.70 (10.85)	4.0 (4.13)	253 (773.94)	54.62	1.80

TABLE 5: Infrared absorption frequencies of oxovanadium(1V) complexes of N[p-(chloro benzalidene) amino] antipyrine morpholino methyl thiourea ($C_{24}H_{27}ON_6SCl$)

Assignments	$C_{24}H_{27}ON_6SCl$	$VOCl_2(C_{24}H_{27}ON_6SCl)$	$VOBr_2(C_{24}H_{27}ON_6SCl)$	$VOI_2(C_{24}H_{27}ON_6SCl)$	$VO(NO_3)_2(C_{24}H_{27}ON_6SCl)$	$VO(NCS)_2(C_{24}H_{27}ON_6SCl)$	$VO(ClO_4)_2(C_{24}H_{27}ON_6SCl).H_2O$
1	2	3	4	5	6	7	8
V(NH)	3440s 3270s	3440m 3265m	3440s 3270s	3430m 3370m	3440s 3270s	3430m 3270m	3435s 3270s
V(C=N)	1600vs	1570m	1570vs	1560m	1570vs	1570m	1570vs
V(C=S)+V(C=N) + V(C-N)	1330s 1300s	1380s 1330m	1370m 1325m	1375m 1310m	1380s 1335m	1160m 1135m	1370s 1325m
$\delta(NCS)$+CS Bending	1120s 1095s	1160m 1130m	1165m 1135w	1160m 1130m	1155m 1130m	1160m 1135m	1150m 1140m
v(N-N)	1050s	1060m	1065m	1060m	1065m	1060m	1065m
v(C=S)	820s 760vs	790s 700m	780s 710m	785m 715s	780m 715w	780m 720m	780s 720m
v(V-N)/v(V-S)	-	360m 320w	355m 315w	360m 320w	340m 310w	345m 315w	350m 310w



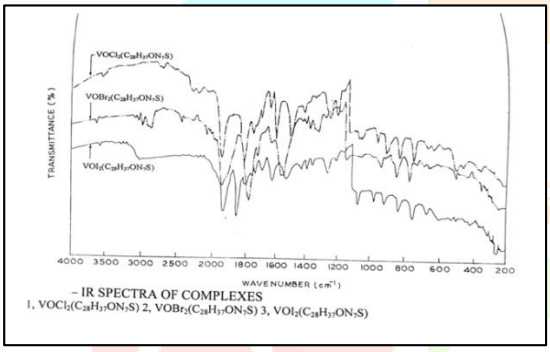
- IR SPECTRA OF COMPLEXES
1, $VOCl_2(C_{24}H_{27}ON_6SCl)$ 2, $VOBr_2(C_{24}H_{27}ON_6SCl)$ 3, $VOI_2(C_{24}H_{27}ON_6SCl)$



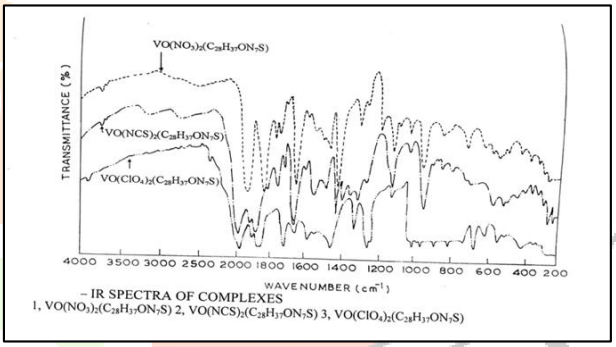
– IR SPECTRA OF COMPLEXES
1, $VO(NO_3)_2(C_{24}H_{27}ON_6SCl)$ 2, $VO(NCS)_2(C_{24}H_{27}ON_6SCl)$ 3, $VO(ClO_4)_2(C_{24}H_{27}ON_6SCl)$

TABLE 6: Infrared absorption frequencies of oxovanadium(1V) complexes of 4[N-(4-Diethyl amino benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{28}H_{37}ON_7S$)

Assignments	$C_{28}H_{37}ON_7S$	$VOCl_2(C_{28}H_{37}ON_7S)$	$VOBr_2(C_{28}H_{37}ON_7S)$	$VOI_2(C_{28}H_{37}ON_7S)$	$VO(NO_3)_2(C_{28}H_{37}ON_7S)$	$VO(NCS)_2(C_{28}H_{37}ON_7S)$	$VO(ClO_4)_2(C_{24}H_{27}ON_6SCl).H_2O$
1	2	3	4	5	6	7	8
V(NH)	3360s 3330s	3350m 3330m	3360s 3335s	3360m 3330m	3360s 3330s	3360m 3330m	3435s 3270s
V(C=N)	1600vs	1565m	1570vs	1565m	1570vs	1570m	1570vs
V(C=S)+V(C=N) + V(C-N)	1310s 1290s	1370s 1335m	1365m 1340m	1374m 1335m	1370s 1340m	1370m 1340m	1370s 1325m
$\delta(NCS)$+CS Bending	1115s 1095s	1170m 1130m	1165m 1130w	1170m 1135m	1160m 1140m	1170m 1135m	1150m 1140m
v(N-N)	1050s	1060m	1065m	1065m	1060m	1060m	1065m
v(C=S)	630s 730vs	780s 710m	770s 705m	775m 710s	775m 715w	780m 720m	780s 720m
v(V-N)/v(V-S)	-	340m 310w	350m 320w	340m 315w	360m 310w	345m 315w	350m 310w



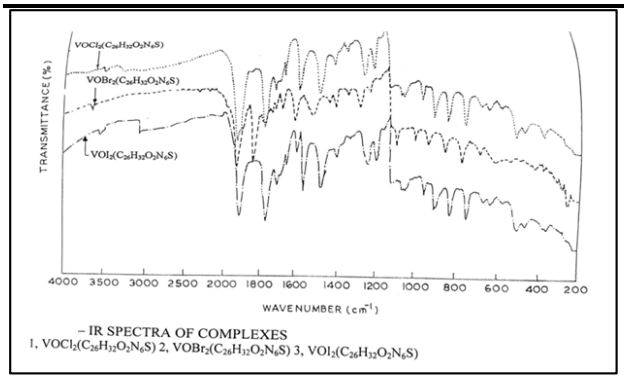
– IR SPECTRA OF COMPLEXES
1, $VOCl_2(C_{28}H_{37}ON_7S)$ 2, $VOBr_2(C_{28}H_{37}ON_7S)$ 3, $VOI_2(C_{28}H_{37}ON_7S)$



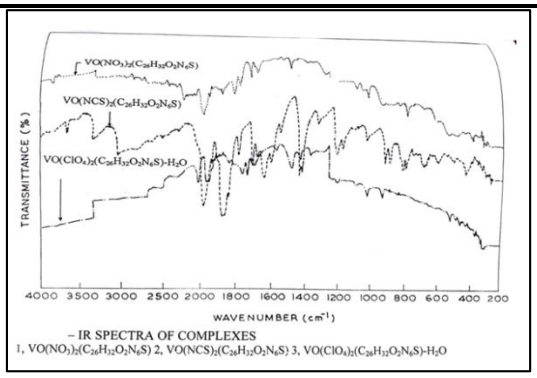
– IR SPECTRA OF COMPLEXES
1, $VO(NO_3)_2(C_{28}H_{37}ON_7S)$ 2, $VO(NCS)_2(C_{28}H_{37}ON_7S)$ 3, $VO(ClO_4)_2(C_{28}H_{37}ON_7S)$

TABLE 7: Infrared absorption frequencies of oxovanadium(1V) complexes of N-[(4-hydroxy-3-ethoxy benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_2N_6S$)

Assignments	$C_{26}H_{32}O_2N_6S$	$VOCl_2(C_{26}H_{32}O_2N_6S)$	$VOBr_2(C_{26}H_{32}O_2N_6S)$	$VOI_2(C_{26}H_{32}O_2N_6S)$	$VO(NO_3)_2(C_{26}H_{32}O_2N_6S)$	$VO(NCS)_2(C_{26}H_{32}O_2N_6S)$	$VO(ClO_4)_2(C_{26}H_{32}O_2N_6S).H_2O$
1	2	3	4	5	6	7	8
V(NH)	3420s 3310s	3420m 3310m	3415s 3310s	3360m 3330m	3420s 3310s	3420m 3310m	3360m 3330m
V(C=N)	1600vs	1570m	1570vs	1575m	1565vs	1570m	1575m
V(C=S)+V(C=N) + V(C-N)	1320s 1195s	1365s 1245m	1365m 1340m	1370m 1250m	1365s 1245m	1365s 1245m	1370m 1250m
$\delta(NCS)$+CS Bending	1120s 1095s	1170m 1125m	1165m 1130w	1170m 1130m	1170m 1125m	1170m 1125m	1170m 1130m
v(N-N)	1060s	1075m	1065m	1070m	1075m	1075m	1070m
v(C=S)	840s 820vs	770s 755m	770s 705m	770m 745s	780m 760w	770s 755m	770m 745s
v(V-N)/v(V-S)	-	350m 315w	350m 320w	340m 320w	340m 320w	350m 315w	340m 320w



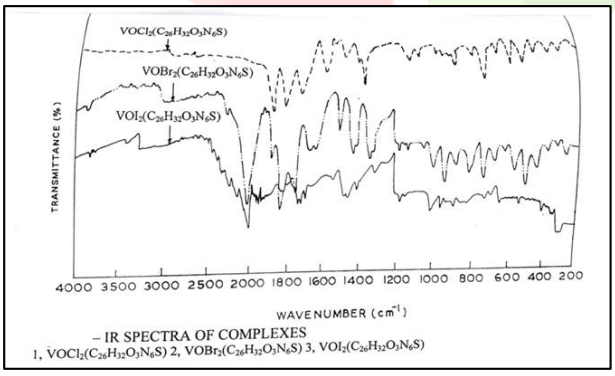
– IR SPECTRA OF COMPLEXES
1, $VOCl_2(C_{26}H_{32}O_2N_6S)$ 2, $VOBr_2(C_{26}H_{32}O_2N_6S)$ 3, $VOI_2(C_{26}H_{32}O_2N_6S)$



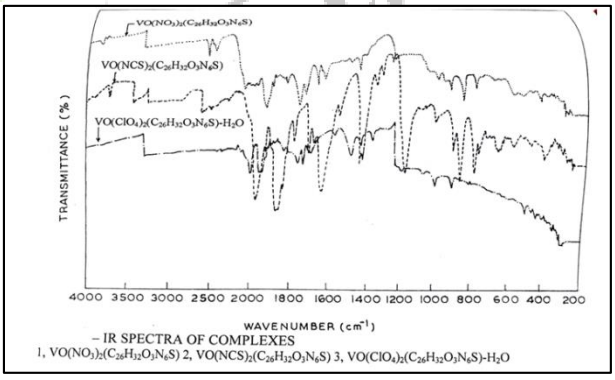
– IR SPECTRA OF COMPLEXES
1, $VO(NO_3)_2(C_{26}H_{32}O_2N_6S)$ 2, $VO(NCS)_2(C_{26}H_{32}O_2N_6S)$ 3, $VO(ClO_4)_2(C_{26}H_{32}O_2N_6S)\text{-}H_2O$

TABLE 8: Infrared absorption frequencies of oxovanadium(1V) complexes of N-[(4-ethoxy benzalidene)amino]antipyrine morpholino methyl thiourea ($C_{24}H_{32}O_3N_6S$)

Assignments	$C_{24}H_{32}O_3N_6S$	$VOCl_2(C_{24}H_{32}O_3N_6S)$	$VOBr_2(C_{24}H_{32}O_3N_6S)$	$VOI_2(C_{24}H_{32}O_3N_6S)$	$VO(NO_3)_2(C_{24}H_{32}O_3N_6S)$	$VO(NCS)_2(C_{24}H_{32}O_3N_6S)$	$VO(ClO_4)_2(C_{24}H_{32}O_3N_6S).H_2O$
1	2	3	4	5	6	7	8
V(NH)	3440s 3280s	3440m 3280m	3440s 3280s	3440m 3280m	3440s 3285s	3440m 3280m	3445m 3280m
V(C=N)	1600vs	1570m	1565vs	1570m	1570vs	1570m	1575m
V(C=S)+V(C=N) + V(C-N)	1315s 1190s	1365s 1200m	1370m 1210m	1360m 1215m	1370s 1215m	1365s 1200m	1370m 1205m
$\delta(NCS)$+CS Bending	1120s 1095s	1160m 1130m	1165m 1130w	1160m 1135m	1160m 1130m	1160m 1135m	1168m 1130m
v(N-N)	1040s	1050m	1055m	1055m	1055m	1055m	1050m
v(C=S)	840s 820m 780s	810s 790m	800s 760m	610m 790s	810m 785w	815s 780m	810m 770s
v(V-N)/v(V-S)	-	340m 315w	350m 320w	340m 320w	355m 310w	350m 320w	340m 315w



– IR SPECTRA OF COMPLEXES
1, $VOCl_2(C_{26}H_{32}O_3N_6S)$ 2, $VOBr_2(C_{26}H_{32}O_3N_6S)$ 3, $VOI_2(C_{26}H_{32}O_3N_6S)$



– IR SPECTRA OF COMPLEXES
1, $VO(NO_3)_2(C_{26}H_{32}O_3N_6S)$ 2, $VO(NCS)_2(C_{26}H_{32}O_3N_6S)$ 3, $VO(ClO_4)_2(C_{26}H_{32}O_3N_6S)\text{-}H_2O$

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5. References:

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