

**Adducts of oxovanadium(IV) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-w-(benzoyl /4-chlorobenzoyl/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methylpyridine**

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**Abstract**

Vanadium (IV) is the most important and stable oxidation state of vanadium. Many vanadium (IV) complexes contain oxovanadium (IV) ( $VO^{2+}$ ) group and form six coordinated and four coordinated oxovanadium compounds.

The compounds may either be mononuclear with a vanadium oxygen double bond or polynuclear with V-O-V-O---bridge bonds. In an octahedral field, the magnetic moment values for oxovanadium(IV) complexes are in the range of 1.73 - 1.85 BM but sometimes very low values of the order of 1.35 - 1.48 B.M. are also observed due to metal-metal interactions within a dimeric molecule.

In the present case, molecular weight determination ruled out the possibility of a dimeric association and the observed magnetic moment values varied from 1.75 to 1.92 B.M. which correspond to the presence of single unpaired electron with little or no orbital contribution to the spin-only magnetic moment value predicting distorted octahedral geometry for oxovanadium(IV) complexes.

**Introduction**

The micro-analytical data and the molar conductance values solution of metal salt with the solution of ligand in the same solvent and corresponding base in 1:1:2 molar ratio followed by refluxing for 2-3 h. The structure elucidation of the isolated adducts was carried out on the basis of same technique as employed for the complexes.

Some of the characteristic absorption frequencies shown by the ligands  $L_I$ - $L_{IV}$  altered on coordination with oxovanadium(IV).

The IR spectra of free ligands exhibited absorption bands in the region  $1645$ - $1615\text{ cm}^{-1}$  due to (C=N) stretching mode of ( $>C=N-C$ ) group which shifted downward to  $1625$ - $1590\text{ cm}^{-1}$  in the spectra of metal complexes suggesting thereby the involvement of imine nitrogen of this group in bond formation with the metal ion, Participation of this imine nitrogen in coordination was further confirmed by the shifting of  $\nu(C-N)$  to  $1320$ - $1305$  and  $1275$ - $1245\text{ cm}^{-1}$  which was observed in the region  $1350$ - $1320$  and  $1290$ - $1260\text{ cm}^{-1}$  in the spectra of parent ligands (Das et al., 1990).

The stretching vibrations due to  $\nu(C=N)$  mode of ( $>C=N-H$ ) group and (N-H) group remained unaltered in the spectra of the metal complexes suggesting thereby the non-participation of the nitrogen of (N-H) groups in coordination, The infrared spectra of the metal complexes exhibited a new band around  $1240$ - $1225\text{ cm}^{-1}$  characteristic of chelate ring vibration (Syamal, 1978).

The presence of coordinated water was confirmed by a broad band in the region  $3450$ - $3400\text{ cm}^{-1}$  due to (O-H) mode in the spectra of complexes (Rana and Shah, 1986).

The spectra of the complexes exhibited ( $\nu=0$ ) vibrations at  $950$ - $940\text{ cm}^{-1}$  (Ray et al. 1965). The appearance of new bands at  $495$ - $490$  and  $460$ - $435\text{ cm}^{-1}$  in the IR spectra of the complexes was attributed to the  $\nu(M-O)$  and  $\nu(M-N)$  vibrations, respectively (Nakamoto, 1978), confirming thereby the coordination through oxygen of water molecule and nitrogen (Ferraro, 1971).

Because of the strong VO bonding in oxovanadium(IV) compounds, the interpretation of the electronic spectra is not as simple as it would be for an ordinary octahedral complex.

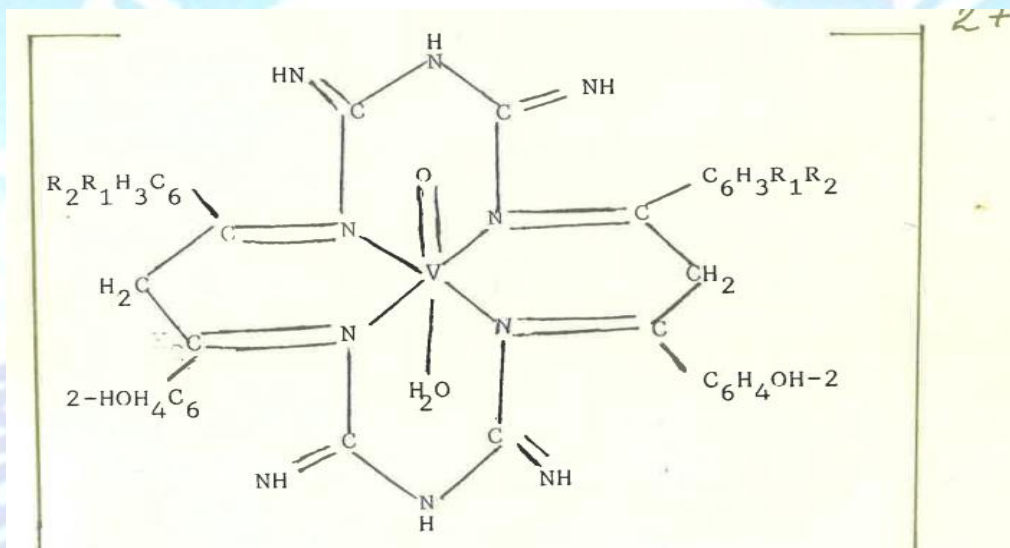
The electronic spectra of vanadyl ion are consistent with the formula  $[VO(H_2O)_5]^{2+}$  (Ballhausen and 1962).

The penta-coordinated complexes take up a sixth ligand quite readily becoming octahedral with donors such as pyridine or triphenylphosphine. The  $\nu=0$  stretching frequency is quite sensitive to the nature of trans Ligand and donors which increase the electron density on the metal thereby

reduce its acceptor properties towards oxygen and hence cause lowering of  $\nu_0$  multiple bond character and hence stretching frequency (Selbin, 1966).

On the basis of micro analytical data, magnetic moment, molecular weight determination and spectral data the complexes have been assigned distorted octahedral geometry with 1:1 metal: ligand stoichiometry.

The ligands acted as tetradentate with the four nitrogen atoms of the Ligand occupying equatorial positions whereas vanadyl oxygen and water occupied axial positions (Ballhausen and Gray, 1962).



### Adducts of oxovanadium(IV) complexes of cyclo(1,2)-dibenzylguanidinyl bis[2-hydroxy-w-(benzoyl /4-chlorobenzoyl/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methylpyridine

The stereochemistry of the adducts has been elucidated on the basis of same techniques as employed for the complexes. It has been found that coordinated water being weaker base is replaced by the stronger heterocyclic base in the adducts. The molar conductance values were in the range of  $75-100 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , suggesting 1:1 electrolytic nature of the adducts. The elemental analysis and molecular weight determination conformed to 1:1 stoichiometry of the adducts.



(i) Infrared spectra

No significant change was observed in the infrared spectra of the adducts and oxovanadium(IV) Complexes. The stretching band due to (C=N) of (>C=N-C) group appearing at 1645-1615  $\text{cm}^{-1}$  in the spectra of the ligands was shifted to lower frequency (1625-1580  $\text{cm}^{-1}$ ) in the spectra of adducts which suggested the involvement of imine nitrogen of this group in bonding. This was further supported by a hypso-chromic shift in the (C-N) bands from 1350-1320  $\text{cm}^{-1}$  and 1290-1260  $\text{cm}^{-1}$  to 1325-1295  $\text{cm}^{-1}$  and 1270-1240  $\text{cm}^{-1}$  in the adducts (Das et al., 1990).

The stretching vibrations due to (C=N) mode of (>C=N-H) group and (N-H) group appearing at 1680-1665 and 3340-3280; 3260-3190  $\text{cm}^{-1}$  respectively in the spectra of free ligands remained unaffected in the spectra of adducts which suggested the non-participation of nitrogen atom of (N-H) groups in complexation.

The new bands appearing in the spectra of the adducts, which were absent in the spectra of ligands, at 1240-1225  $\text{cm}^{-1}$  and 465-435  $\text{cm}^{-1}$  were assigned to the chelate ring vibration (Syamal, 1978) and (M-N) vibrations, respectively.

The absorption frequency characteristic of (O-H) mode observed at 3450-3400  $\text{cm}^{-1}$  in the spectra of the oxovanadium(IV) complexes was absent in the IR spectra of the adducts indicating the replacement of coordinated water molecule in oxovanadium(IV) complex by the base molecule in the adducts. This was further supported by the absence of a band at 495-490  $\text{cm}^{-1}$  due to Y(M-O) stretching.

The  $\nu=0$  stretching frequencies of the adducts were in range 955-945  $\text{cm}^{-1}$  (Ray et al., 1965). Earlier studies by Ballhausen and Gray (1962) also indicated that in vanadyl complexes the axial water molecule is weakly bound and can be easily replaced by a strong base.

(ii) Magnetic moment and electronic spectra

The effective magnetic moment values of the adducts of oxovanadium(IV) complexes at 25°C were found to be range of 1.74 to 1.90 B.M. which correspond to the presence of a single unpaired electron, with little or no orbital contribution to the spin-only magnetic moment value,

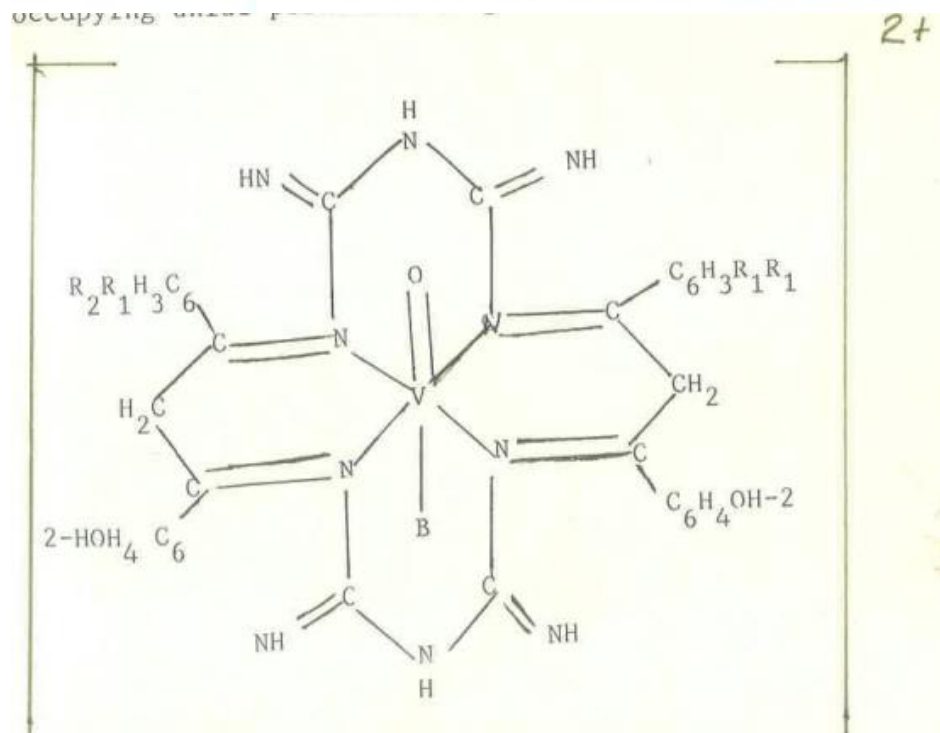
suggesting an octahedral geometry for the adducts of oxovanadium(IV) complexes (Ballhausen, 1962).

The electronic spectra of the adducts of Oxovanadium(IV) complexes exhibited two bands in the region  $12980-13750\text{ cm}^{-1}$  and  $17050-17540\text{ cm}^{-1}$  assigned to corresponding transitions, respectively confirming Octahedral geometry for the adducts (Ballhausen and Gray,1962)

The crystal field splitting energy ( $10 Dq$ )  $17050-17540\text{ cm}^{-1}$  and field stabilization energy  $244.73 - 253.06\text{ K J mol}^{-1}$  also confirmed distorted octahedral geometry of the base adducts of oxovanadium(IV) complexes (Ballhausen, 1962).

On the basis of elemental analysis, molecular weight determination and spectral data distorted octahedral geometry was proposed for the adducts of oxovanadium(IV) complexes having 1:1 metal: ligand stoichiometric ratio.

The ligand acted as tetradentate with four donor nitrogen atoms of the ligand at equatorial positions and base and vanadyl oxygen occupying axial positions.



**RESULTS**

Table : Physical and analytical data of oxovanadium(IV) complexes of cyclo(1,2)-dibiguaniidynyl bis[2-hydroxy-*p*-(benzoyl /4-chlorobenzoyl)acetophenone](L<sub>I</sub> and L<sub>II</sub>) and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular weight
			C	H	N	S/Cl	M	
[Vo(L <sub>I</sub> )(H <sub>2</sub> O)]So <sub>4</sub>	C <sub>34</sub> H <sub>32</sub> N <sub>10</sub> O <sub>8</sub> SV	74	50.81 (51.58)	4.00 (4.04)	17.68 (17.70)	4.00 (4.04)	6.21 (6.43)	782.0 (790.9)
[Vo(L <sub>I</sub> )(Py)]So <sub>4</sub>	C <sub>39</sub> H <sub>35</sub> N <sub>11</sub> O <sub>7</sub> SV	68	54.14 (54.93)	4.06 (4.10)	18.00 (18.07)	3.62 (3.75)	5.19 (5.97)	847.0 (851.9)
[Vo(L <sub>I</sub> )(2-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>37</sub> N <sub>11</sub> O <sub>7</sub> SV	63	55.37 (55.43)	4.12 (4.27)	17.12 (17.78)	3.64 (3.69)	5.53 (5.87)	860.0 (865.9)
[Vo(L <sub>I</sub> )(4-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>37</sub> N <sub>11</sub> O <sub>7</sub> SV	64	55.13 (55.43)	4.09 (4.27)	17.23 (17.78)	3.62 (3.69)	5.48 (5.87)	854.0 (865.9)
[Vo(L <sub>II</sub> )(H <sub>2</sub> O)]So <sub>4</sub>	C <sub>34</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>10</sub> O <sub>8</sub> SV	67	47.09 (47.55)	3.18 (3.49)	16.04 (16.29)	3.69/8.16 (3.72)/(8.26)	5.41 (5.92)	850.0 (858.9)
[Vo(L <sub>II</sub> )(Py)]So <sub>4</sub>	C <sub>39</sub> H <sub>33</sub> Cl <sub>2</sub> N <sub>11</sub> O <sub>7</sub> SV	71	50.79 (50.92)	3.24 (3.59)	16.63 (16.74)	3.40/7.52 (3.47)/(7.71)	5.26 (5.53)	904.0 (919.9)
[Vo(L <sub>II</sub> )(2-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>35</sub> Cl <sub>2</sub> N <sub>11</sub> O <sub>7</sub> SV	71	52.13 (52.23)	3.29 (3.75)	16.26 (16.48)	3.37 / 7.49 (3.42)/(7.60)	5.13 (5.45)	927.0 (933.9)
[Vo(L <sub>II</sub> )(4-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>35</sub> Cl <sub>2</sub> N <sub>11</sub> O <sub>7</sub> SV	71	52.19 (52.23)	3.13 (3.75)	16.12 (16.48)	3.35 / 7.46 (3.42)/(7.60)	5.24 (5.45)	921.0 (933.9)

Table : Physical and analytical data of oxovanadium (IV) complexes of cyclo(1,2)-dibiguaniidynyl bis[2-hydroxy-*m*-(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] (L<sub>III</sub> and L<sub>IV</sub>) and their adducts

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular weight
			C	H	N	S	M	
[Vo(L <sub>III</sub> )(H <sub>2</sub> O)]So <sub>4</sub>	C <sub>34</sub> H <sub>30</sub> N <sub>12</sub> O <sub>12</sub> SV	72	46.00 (46.31)	3.18 (3.40)	19.00 (19.07)	3.59 (3.63)	5.11 (5.77)	871.0 (880.9)
[Vo(L <sub>III</sub> )(Py)]So <sub>4</sub>	C <sub>39</sub> H <sub>33</sub> N <sub>13</sub> O <sub>11</sub> SV	70	48.91 (49.68)	3.42 (3.50)	19.21 (19.32)	3.26 (3.39)	5.23 (5.40)	930.0 (941.9)
[Vo(L <sub>III</sub> )(2-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>35</sub> N <sub>13</sub> O <sub>11</sub> SV	70	50.11 (50.21)	4.13 (4.18)	18.66 (19.03)	3.13 (3.34)	5.19 (5.32)	942.0 (955.9)
[Vo(L <sub>III</sub> )(4-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>35</sub> N <sub>13</sub> O <sub>11</sub> SV	70	50.20 (50.21)	4.00 (4.18)	18.95 (19.03)	3.17 (3.34)	5.14 (5.32)	945.0 (955.9)
[Vo(L <sub>IV</sub> )(H <sub>2</sub> O)]So <sub>4</sub>	C <sub>34</sub> H <sub>28</sub> N <sub>14</sub> O <sub>16</sub> SV	68	42.00 (42.02)	2.16 (2.88)	19.99 (20.18)	3.20 (3.29)	5.16 (5.24)	961.0 (970.9)
[Vo(L <sub>IV</sub> )(Py)]So <sub>4</sub>	C <sub>39</sub> H <sub>31</sub> N <sub>15</sub> O <sub>15</sub> SV	64	45.10 (45.35)	2.78 (3.00)	20.01 (20.35)	3.01 (3.10)	4.77 (4.93)	1025.0 (1031.9)
[Vo(L <sub>IV</sub> )(2-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>33</sub> N <sub>15</sub> O <sub>15</sub> SV	60	45.19 (45.89)	3.13 (3.15)	20.00 (20.07)	2.76 (2.86)	4.61 (4.86)	1038.0 (1045.9)
[Vo(L <sub>IV</sub> )(4-Me-Py)]So <sub>4</sub>	C <sub>40</sub> H <sub>33</sub> N <sub>15</sub> O <sub>15</sub> SV	65	45.39 (45.89)	3.11 (3.15)	19.82 (20.07)	2.76 (2.86)	4.73 (4.86)	1040.0 (1045.9)



Table : Infrared spectral characteristics of oxovanadium(IV) complexes of cyclo(1,2)-dibiguanidiny bis[2-hydroxy- $\psi$ -(benzoyl/4-chlorobenzoyl) acetophenone] ( $L_I$  and  $L_{II}$ ) and their adducts.

Compound	Assignments ( $cm^{-1}$ )							
	$\nu(N-H)$	$\nu(C=N)$ of ( $>C=N-H$ )	$\nu(C=N)$ of ( $>C=N-C$ )	$\nu(C-N)$	Chelate ring vibration	$\nu(V=O)$	$\nu(M-O)$	$\nu(M-N)$
$[Vo(L_I)(H_2O)]So_4$	3320,3190	1680	1590	1320,1250	1230	940	495	460
$[Vo(L_I)(Py)]So_4$	3320,3190	1680	1595	1320,1250	1240	945	-	460
$[Vo(L_I)(2-Me-Py)]So_4$	3320,3190	1680	1590	1325,1260	1230	955	-	455
$[Vo(L_I)(4-Me-Py)]So_4$	3320,3190	1680	1600	1315,1255	1235	950	-	465
$[Vo(L_{II})(H_2O)]So_4$	3340,3260	1665	1595	1310,1260	1225	950	495	435
$[Vo(L_{II})(Py)]So_4$	3340,3260	1665	1580	1325,1255	1232	948	-	445
$[Vo(L_{II})(2-Me-Py)]So_4$	3340,3260	1665	1590	1300,1245	1230	948	-	440
$[Vo(L_{II})(4-Me-Py)]So_4$	3340,3260	1665	1580	1325,1250	1230	950	-	435

Table : Infrared spectral characteristics of oxovanadium(IV) complexes of cyclo(1,2)-dibiguanidiny bis[2-hydroxy- $\psi$ -(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] ( $L_{III}$  and  $L_{IV}$ ) and their adducts.

Compound	Assignments ( $cm^{-1}$ )							
	$\nu(N-H)$	$\nu(C=N)$ of ( $>C=N-H$ )	$\nu(C=N)$ of ( $>C=N-C$ )	$\nu(C-N)$	Chelate ring vibration	$\nu(V=O)$	$\nu(M-O)$	$\nu(M-N)$
$[Vo(L_{III})(H_2O)]So_4$	3300,3210	1665	1615	1305,1245	1230	945	495	450
$[Vo(L_{III})(Py)]So_4$	3300,3210	1665	1600	1300,1245	1230	945	-	445
$[Vo(L_{III})(2-Me-Py)]So_4$	3300,3210	1665	1605	1295,1240	1225	940	-	445
$[Vo(L_{III})(4-Me-Py)]So_4$	3300,3210	1665	1600	1310,1250	1235	950	-	435
$[Vo(L_{IV})(H_2O)]So_4$	3280,3190	1670	1625	1320,1275	1240	945	490	450
$[Vo(L_{IV})(Py)]So_4$	3280,3190	1670	1620	1320,1270	1235	940	-	460
$[Vo(L_{IV})(2-Me-Py)]So_4$	3280,3190	1670	1620	1315,1270	1235	940	-	455
$[Vo(L_{IV})(4-Me-Py)]So_4$	3280,3190	1670	1625	1315,1265	1232	945	-	450

Table : Magnetic moment, electronic spectral and molar conductance data of oxovanadium (IV) complexes of cyclo(1,2)-dibiguanidinyl bis(2-hydroxy-*m*-(benzoyl/4-chlorobenzoyl)acetophenone) ( $L_I$  and  $L_{II}$ ) and their adducts.

Compound	${}^2B_2 \rightarrow {}^2E$ ( $cm^{-1}$ )	${}^2B_2 \rightarrow {}^2B_1$ ( $cm^{-1}$ )	10 Dq ( $cm^{-1}$ )	LFSE ( $KJ mol^{-1}$ )	$\mu_{eff}$ (B.M.)	Molar conductance ( $ohm^{-1}cm^2mol^{-1}$ )
$[Vo(L_I)(H_2O)]So_4$	13900	17630	17630	253.06	1.75	85
$[Vo(L_I)(Py)]So_4$	13750	17540	17540	251.77	1.78	95
$[Vo(L_I)(2-Me-Py)]So_4$	13200	17520	17520	251.48	1.74	100
$[Vo(L_I)(4-Me-Py)]So_4$	12980	17500	17500	251.19	1.75	75
$[Vo(L_{II})(H_2O)]So_4$	13200	17120	17120	245.74	1.81	95
$[Vo(L_{II})(Py)]So_4$	13320	17150	17150	246.17	1.83	88
$[Vo(L_{II})(2-Me-Py)]So_4$	13140	17210	17210	247.03	1.80	94
$[Vo(L_{II})(4-Me-Py)]So_4$	13430	17135	17135	245.95	1.80	82

Table : Magnetic moment, electronic spectral and molar conductance data of oxovanadium(IV) complexes of cyclo(1,2)-dibiguanidinyl bis(2-hydroxy-*m*-(3-nitrobenzoyl/3,5-dinitrobenzoyl)acetophenone) ( $L_{III}$  and  $L_{IV}$ ) and their adducts.

Compound	${}^2B_2 \rightarrow {}^2E$ ( $cm^{-1}$ )	${}^2B_2 \rightarrow {}^2B_1$ ( $cm^{-1}$ )	10 Dq ( $cm^{-1}$ )	LFSE ( $KJ mol^{-1}$ )	$\mu_{eff}$ (B.M.)	Molar conductance ( $ohm^{-1}cm^2mol^{-1}$ )
$[Vo(L_{III})(H_2O)]So_4$	12300	17250	17250	247.60	1.89	95
$[Vo(L_{III})(Py)]So_4$	13500	17320	17320	248.61	1.86	90
$[Vo(L_{III})(2-Me-Py)]So_4$	13600	17240	17240	247.46	1.90	100
$[Vo(L_{III})(4-Me-Py)]So_4$	17710	17150	17150	246.17	1.83	90
$[Vo(L_{IV})(H_2O)]So_4$	13220	17150	17150	246.17	1.92	85
$[Vo(L_{IV})(Py)]So_4$	13100	17200	17200	246.88	1.85	94
$[Vo(L_{IV})(2-Me-Py)]So_4$	13600	17050	17050	244.73	1.82	86
$[Vo(L_{IV})(4-Me-Py)]So_4$	13300	17210	17210	247.03	1.84	92



## CONCLUSION

All the adducts were colored and insoluble in most of the organic solvents except DMSO and DMF. The molar conductance values indicated their 1:1 or 4:2 electrolytic nature while molecular weight data suggested their monomeric behaviour.

The elemental analysis and molecular weight data indicated the formation of 1:1 metal: ligand complexes. Molar conductance values ( $85-95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in dry DMSO at  $25^\circ\text{C}$  corresponded to 1:1 electrolytic nature of the complexes.

The stereochemistry of the complexes has been elucidated on the basis of their magnetic moment and electronic and infrared spectral data.

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