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SYNTHESIS OF N-SUBSTITUTED -N'-ARYL (SUBSTITUTED) THIO UREAS AND THEIR VANADIUM(V) OXYTRI-CHLORIDE COMPLEXES

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New vanadium (V) oxytrichloride complexes with some N-substituted -N'-aryl (substituted) thio ureas have been prepared. The complexes are of the type $VOCl_3.L$ where L, is a molecule of bidentate ligand. The complexes have been characterised on the basis of elemental analysis, molar conductance, magnetic susceptibility and infra-red spectral studies. The co-ordination of ligand to metal through thioketo sulphur atom and nitrogen of -NH group with octahedral configuration has been suggested.

Key Words : Vanadyl (V) Chloride Complexes; N-substituted-N'-Aryl (substituted) Thio Ureas

INTRODUCTION

A number of the addition and substitution products of $VOCl_3$ have been reported[1,2] with organic substances in inert organic solvents. Reduction of $VOCl_3$ has also been observed[3,4] by many carboxylic acids with concomitant solvolysis to produce vanadyl (IV) carboxylates. Aliphatic amines and thioethers are also known[5] to have reduced $VOCl_3$ with the formation of $VOCl_2.2L$ type complexes, where L pertains to CH_3NH_2, $(CH_3)_2S$ and $(C_2H_5)_2S$. Some $VOCl_2(OR)$. $VOCl(OR)_2$ and $VOCl(OPh)_2$ type chloroalkoxides of $VOCl_3$ have also been synthesized. With aniline, $VOCl_3$ has been reported[7] to form $VO(NHPh)_3$ type complexes. Some unreduced $VOCl_3.2L$ type complexes have also been studied[8,9] with aromatic amines.

From a critical survey of literature it has been found that almost no work has been done on the complexation of $VOCl_3$ with nitrogen and sulphur containing polydentate ligands. Our studies are therefore attributed to the isolation and characterization of $VOCl_3$ complexes with N-substituted-N'-aryl (substituted) thio ureas.

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EXPERIMENTAL

The chemicals used were of either BDH "AnalaR" or E. MERCK grade reagent quality. All the solvents were purified by repeated distillation after drying appropriately.

Vanadium (V) oxytrichloride was prepared by refluxing mixture of $SOCl_2$ and V_2O_5 under rigorous anhydrous conditions.[10] The product was distilled (125-127 °C) and purity was checked by elemental analysis. Results are reported in Table I.

Synthesis of Ligands

All the ligands were prepared by the known method.[11] Equimolar amounts of the amine and mustard oil (phenyl, *o*-tolyl or *p*-tolyl isothiocyanate) were taken in ethanol. Mixture was refluxed for 3-4hr. The substituted thiourea started separating out even in the warm ethanol. It was filtered, washed with a little ether and dilute alcohol and finally recrystallized from absolute ethanol. Their formation can be represented as follows:-

$$R.\ NH_2 + R'.N:C:S \rightarrow R.NH.(CS).NH.R'$$

Amine Mustard oil N-substituted-N'-aryl (substituted) thio urea

where (the ligands under investigation are):-

(*a*) R' = Phenyl and R = (I) Benzyl (Bz. PTU), (II) *p*-acetanilide (*p*-ACNLD. PTU), (III) Phenyl (DPTU), (IV) *o*-Tolyl (*o*-T.PTU), (V) *p*-Tolyl (*p*-T.PTU), (VI) *m*-Tolyl (*m*-T.PTU), (VII) *o*-Anisyl (*o*-An. PTU), (VIII) *p*-Anisyl (*p*-An. PTU), (IX) *m*-Anisyl (*m*-An.PTU), (X) *o*-Phenetyl (*o*-Pn.PTU), (XI) *p*-phenetyl (*p*-Pn.PSU), (XII) *m*-Phenetyl (*m*-Pn.PTU), (XIII) α-Naphthyl (α-Np.PTU), (XIV) β-Naphthyl (β-Np.PTU), (XV) Methyl (Me.PTU), (XVI) Ethyl (Et.PTU), (XVII) *n*-Hexyl (*n*-Hex.PTU).

(b) R' = *o*-Tolyl and R = (XVIII) Phenyl (p.*o*-TTU), (XIX) Benzyl (Bz.*o*-TTU), (XX) Tolyl (D. *o*-TTU), (XXI) *p*-Tolyl (*p*-T.*o*-TTU), (XXII) *m*-Tolyl (*m*-T. *o*-TTU), (XXIII) *o*-Anisyl (*o*-An.*o*-TTU), (XXIV) *p*-Anisyl (*p*-An.*o*.TTU), (XXV) *o*-Phenetyl (*o*-Pn. *o*-TTU), (XXVI) *p*-Phenetyl (*p*-Pn. *o*-TTU), (XXVII) α-Naphthyl (α-Np.*o*-TTU);

(c) R' = *p*-Tolyl and R = (XXVIII) Phenyl (Ph.*p*-TTU), (XXIX) Benzyl (Bz.*p*-TTU), (XXX) *p*-Tolyl (D.*p*-TTU), (XXXI) *p*-Anisyl (*p*-An.*p*-TTU), (XXXII) β-Naphthyl (β-Np.*p*-TTU), (XXXIII) Phenyl hydrazine (Diphenyl thiosemi carbazide: DPTSCAZ).

Purity of ligands was checked by their sharp melting points and elemental analysis (Table I).

TABLE I

Colour, melting point and analytical data

SUBSTANCE	M. Pt. °C	COLOUR	ANALYSIS OF THE METAL COMPLEX					
			% Found			% Calculated		
			V	S	Cl	V	S	Cl
$VOCl_3$	—	Reddish yellow	29.48	—	62.01	29.39	—	61.36
$VOCl_3$.Bz.PTU	72	Green	12.67	7.52	24.51	12.26	7.70	25.60
$VOCl_3$.*p*-ACNLD.PTU	67	Green	11.29	6.85	24.01	11.10	6.97	23.19
$VOCl_3$.DPTU	87	Green	12.32	7.02	26.12	12.68	7.96	26.48
$VOCl_3$.*o*-T.PTU	78	Dark green	11.96	8.20	24.99	12.26	7.70	25.60
$VOCl_3$.*p*-T.PTU	77	Dark green	12.02	7.49	26.10	12.26	7.70	25.60
$VOCl_3$.*m*-T.PTU	81	Green	12.96	7.53	25.20	12.26	7.70	25.60
$VOCl_3$.*o*-An.PTU	76	Golden	11.39	7.39	23.98	11.80	7.41	24.64
$VOCl_3$.*p*-An.PTU	84	Dark violet	11.93	7.85	24.94	11.80	7.41	24.64
$VOCl_3$.*m*-An.PTU	88	Green	11.98	8.20	25.01	11.80	7.41	24.64
$VOCl_3$.*o*-Pn.PTU	79	Light green	11.93	7.39	24.21	11.43	7.18	23.86
$VOCl_3$.*p*-Pn.PTU	70	Light green	11.22	7.98	24.12	11.43	7.18	23.86
$VOCl_3$.*m*-Pn.PTU	85	Green	12.04	7.94	24.01	11.43	7.18	23.86
$VOCl_3$.α-Np.PTU	69	Blackish blue	11.01	6.98	24.32	11.28	7.08	22.54
$VOCl_3$.β-Np-PTU	73	Dark blue	11.43	7.23	23.97	11.28	7.08	23.54
$VOCl_3$.Me.PTU	69	Light blue	14.90	9.93	30.98	15.00	9.42	31.32
$VOCl_3$.Et.PTU	62	Light blue	14.54	9.98	29.90	14.41	9.05	30.08
$VOCl_3$.*n*-Hex.PTU			NO PRECIPITATE WAS OBTAINED					
$VOCl_3$.P.*o*-TTU	122	Bluish green	12.22	7.97	26.01	12.26	7.70	25.60
$VOCl_3$.Bz.*o*-TTU	72	Bluish green	11.98	7.84	23.98	11.85	7.44	24.75
$VOCl_3$.D.*o*-TTU	82	Dark green	11.48	7.96	24.98	11.85	7.44	24.75
$VOCl_3$.*p*-T.*o*-TTU	86	Green	11.05	7.04	25.20	11.85	7.44	24.75
$VOCl_3$.*m*-T.*o*-TTU	79	Green	12.01	8.12	25.20	11.85	7.44	24.75
$VOCl_3$.*o*-An.*o*-TTU	81	Dark green	10.98	6.93	24.12	11.43	7.18	23.86
$VOCl_3$.*p*-An.*o*-TTU	79	Dark green	10.89	7.39	23.94	11.43	7.18	23.86
$VOCl_3$.*o*-Pn.*o*-TTU	84	Green	11.00	6.74	24.10	11.08	6.96	23.14
$VOCl_3$.*p*-Pn.*o*-TTU	80	Light green	10.88	6.70	23.19	11.08	6.96	23.14
$VOCl_3$.α-Np.*o*-TTV	134	Green	10.48	6.53	25.07	10.94	6.87	22.84
$VOCl_3$.P.*p*-TTU	82	Green	12.01	7.65	25.07	12.26	7.70	25.60
$VOCl_3$.Bz.*p*-TTU	78	Light green	12.15	8.02	25.12	11.85	7.44	24.75
$VOCl_3$.D.*p*-TTU	89	Light green	12.00	7.68	25.20	11.85	7.44	24.75
$VOCl_3$.*p*-An.*p*-TTU	72	Green	12.03	7.08	24.08	11.43	7.18	23.86
$VOCl_3$.*p*-An.*p*-TTU	122	Green	11.24	7.12	23.12	10.94	6.87	22.84
$VOCl_3$.DPTSCAZ	88	Chocolate	12.02	7.94	26.42	12.22	7.68	25.52

Preparation of the Complexes

All operations were carried out in a dry box. Requisite amount of ligand was dissolved in minimum (~5c.c.) of chloroform and then 0.02M solution was made by adding CCl_4. $VOCl_3$ solution in carbon-tetrachloride (0.03M) was added drop by drop to the ice-cold solution of ligand, maintaining in each case a slight excess of ligand. During the course of reaction, temperature was maintained below 10 °C. The mixture was frequently shaken and allowed to stand for five hours to attain an equilibrium. The coloured complex was filtered, dried and analysed for vanadium, chloride and sulphur.[12]

Instrumentation

Melting points were determined on a unimelt temperature apparatus. The magnetic measurements of complexes were carried out on Gouy balance using a field strength of 5.0×10^3 Gauss and mercury tetrathiocyanato-cobaltate as standard. Molar conductance of the complexes was determined in N,N-dimethyl formamide (DMF) at a concentration of 10^{-3}M with conductivity meter type LBR of Wissenschaftlich technisch, Wersstatten, Germany, using a dip type cell (Table II). The infrared spectra of the ligands and complexes were taken in KBr pellets on infrared spectrophotometer model Backman-20. The important peaks are listed in Tables III and IV.

Results and Discussion

Table I records the analytical data, melting points and colour of complexes. Analytical results correspond to the general empirical formula $VOCl_3$. L, where L is a molecule of ligand.

The molar conductance values (Table II) are in the range of 26.14–74.01 Mhos which are well below those for 1 : 1 electrolyte.[13] The measured values are seem to be due to the partial replacement of chloride by solvent (DMF) molecule. The observed values of magnetic susceptibility (Table II) are in the (negative) range of -0.099 to -0.082×10^{-6} which accounts that all the complexes are diamagnetic.

Important infrared spectral peaks of ligands and complexes are listed in Tables III and IV respectively. In ligands a medium broad band appearing ~3300–3400 may be due to the stretching of –NH group.[14] On complexation this band is shifted to the lower frequency region which infers the co-ordination of -NH group to the vanadium metal atom. Sharp and strong bands ~ 1580cm^{-1} in ligands are assigned to the ν(CN) coupled with —NH deformation vibrations.[15] Lowering of this band by 15–25cm^{-1} on complexation further supports co-ordination of –NH group nitrogen to the vanadium.

The C = S stretching vibrations in ligands appear ~ 740cm^{-1} and ~ 1320cm^{-1} however both contain contribution from ν(CN) vibrations.[15,16]. Both these bands on complexation are shifted down by 20–30cm^{-1} with reduced intensity which indicates the ligand co-ordination to vanadium metal through thioketo sulphur

TABLE II

Magnetic susceptibility and molar conductance results of the complexes

Complex	Magnetic susceptibility $\times 10^{-6}$	Molar Conductance	
		Molarity (M)	Conductance (Mhos)
$VOCl_3$.(Bz.PTU)	—0.4229	0.11×10^{-2}	67.74
$VOCl_3$.(ACNLD.PTU)	—0.3142	0.09×10^{-2}	67.17
$VOCl_3$.(DPTU)	—0.1403	0.13×10^{-2}	71.65
$VOCl_3$.(*o*-TPTU)	—0.2917	0.10×10^{-2}	37.15
$VOCl_3$.(*p*-TPTU)	—0.2881	0.11×10^{-3}	70.95
$VOCl_3$.(*m*-T.PTU)	—0.1935	0.11×10^{-2}	36.77
$VOCl_3$.(*o*-An.PTU)	—0.1466	0.09×10^{-2}	69.66
$VOCl_3$.(*p*-An.PTU)	0.1683	0.11×11^{-2}	70.94
$VOCl_3$.-(*m*An.PTU)	—0.1394	0.10×10^{-2}	71.19
$VOCl_3$.(*o*-Pn.PTU)	—0.1583	0.09×10^{-2}	71.19
$VOCl_3$.(*p*-Pn.PTU)	—0.1046	0.10×10^{-3}	61.82
$VOCl_3$.(*m*-Pn.PTU)	—0.0990	0.09×10^{-2}	42.19
$VOCl_3$.(α-Np.PTU)	—0.3443	0.12×10^{-2}	67.30
$VOCl_3$.(β-Np.PTU)	—0.1641	0.10×10^{-2}	36.40
$VOCl_3$.(Me.PTU)	—0.0996	0.11×10^{-2}	67.84
$VOCl_3$.(Et.PTU)	—0.1390	0.09×10^{-2}	51.85
$VOCl_3$.(p.*o*-TTU)	—0.1781	0.11×10^{-2}	28.97
$VOCl_3$.(D.*o*-TTU)	—0.7141	0.09×10^{-2}	59.46
$VOCl_3$.(*p*-T.*o*-TTU)	—0.5420	0.09×10^{-2}	61.21
$VOCl_3$.(*m*-T.*o*-TTU)	—0.6149	0.10×10^{-2}	46.71
$VOCl_3$.(*o*-An.*o*-TTU)	—0.1810	0.08×10^{-2}	74.01
$VOCl_3$.(*p*-An.*o*-TTU)	—0.2134	0.08×10^{-2}	61.37
$VOCl_3$.(*o*-Pn.*o*-TTU)	0.1301	0.90×10^{-3}	41.94
$VOCl_3$.(*p*-Pn.*o*-TTU)	—0.2114	0.11×10^{-2}	39.18
$VOCl_3$.(α-Np.*o*-TTU)	—0.3191	0.09×10^{-2}	69.67
$VOCl_3$.(Bz.*o*-TTU)	—0.8252	0.08×10^{-2}	70.31
$VOCl_3$.(P. *p*-TTU)	—0.1821	0.12×10^{-2}	30.12
$VOCl_3$.(Bz. *p*-TTU)	—0.2811	0.10×10^{-2}	26.14
$VOCl_3$.(D. *p*-TTU)	—0.5796	0.09×10^{-2}	56.94
$VOCl_3$.(*p*.An. *p*-TTU)	—0.1281	0.09×10^{-2}	65.02
$VOCl_3$.(β-Np. *p*-TTU)	—0.4131	0.12×10^{-2}	31.94
$VOCl_3$.(DPTSCAZ)	—0.1572	0.11×10^{-2}	67.74

atom. The bonds $\sim 1450cm^{-1}$ in ligands are assigned to the NH — C = S group vibrations which is the combination of ν(N–C–N), ν(C=S) and and –NH rocking vibrations.[16,17] The change in the nature of these vibrations on complexation further confirms the ligand co-ordination through thio keto sulphur atom. The possibility of thionethiol tautomerism (H-N-C = S ⇌ N-C = SH) in these ligands has been completely ruled out, for no band around $2500\text{-}2650cm^{-1}$.

The ν(V = O) vibrations in the complexes appear around $1030\text{-}1060cm^{-1}$. These bands are medium and sharp in intensity and are in the region expected for V = O

TABLE III

IR spectral data of ligands and tentative assignments (cm^{-1})

Ligand	(N–H) Stretch	(N–H) Deformation	(C–N) Stretch + Ring Vibration	(C=S) Stretch	(CS + CN) Stretch	(NH–C'=S) Stretch
Bz.PTU	3360*s*	1580*m*	1240*s*	730*m*	1350*s*	1450*s*
p-ACNLD.PTU	3235–3280*ab*	1603*s*	1240*s*	730*m*	1320*s*	1450*m*
DPTU	3190–3220*s*	1600*mb*	1245*m*	750*m*	1320*m*	1455*m*
o-T.PTU	3200–3110*sb*	1600*s*	1260*m*	760*s*	1330*w*	1460*s*
p-T.PTU	3100–3160*sb*	1600*m*	1250*s*	750*s*	1320*s*	1445*s*
m-T.PTU	3180–3200*mb*	1630*s*	1250*s*	750*s*	1320*s*	1450*s*
o-An.PTU	3200–3240*sb*	1605*wb*	1250*s*	750*w*	1335*mb*	1470*m*
p-An.PTU	3180–3300*sb*	1610*wb*	1250*s*	760*w*	1340*m*	1480*s*
m-An.PTU	3300*s*	1600*w*	1250*s*	760*s*	1360*s*	1465*s*
o-Pn.PTU	3160–3210*sb*	1590*s*	1200*s*	745*m*	1360*mb*	1490*sb*
p-PN-PTU	3100–3200*mb*	1600*w*	1220*s*	750*m*	1320*m*	1485*s*
m-Pn.PTU	3180–3300*mb*	1600*s*	1200*m*	740*s*	1360*s*	1490*s*
α-Np.PTU	3260*s*	1590*m*	1260*s*	760*s*	1380*m*	1485*s*
β-Np.PTU	3265*sb*	1595*m*	1260*s*	750*s*	1380*m*	1475*s*
Me.PTU	3090–3170*sb*	1500–1510*sb*	1245*s*	720*s*	1350*mb*	1490*s*
Et.PTU	3190–3210*mb*	1590*s*	1260*m*	740*s*	1350*m*	1490*s*
P.*o*-TTU	3190–3230*sb*	1610*s*	1260*s*	750*s*	1330*s*	1450*m*
Bz.*o*-TTU	3360*s*	1580*w*	1250*s*	760*m*, 740*s*	1345*m*	1500*s*
D.*o*-TTU	3105–3300*sb*	1620*s*	1245*s*	760*s*	1350*s*	1480*s*
p-T.*o*-TTU	3060–3200*sb*	1590*s*	1240*s*	750*m*	1410*s*	1480*sb*
m-T.*o*-TTU	3220–3270*mb*	1595	1245*s*	750*m*	1380*m*	1490*s*
o-An.*o*-TTU	3000–3240*s*	1610*m*	1250*s*	760*w*, 730*s*	1330*s*	1545*sb*
p-An.*o*-TTU	3200–3340*sb*	1620*m*	1250*s*	730*s*	1320*m*	1540*sb*
o-Pn.*o*TTU	3200–3250*mb*	1600*w*	1200*m*	740*m*	1320*s*	1480*s*
p-Pn.*o*-TTU	3400–3480*mb*,3360*s*	1605*m*	1210*m*	740*m*	1320*s*	1500*s*
α-Np.*o*-TTU	3400–3460*mb*	1600*w*	1240*m*, 1270*s*	735*m*	1320*m*	1500*s*
P.*p*-TTU	3300–3340*mb*	1600*s*	1250*s*	750*m*	1320*s*	1445*w*
Bz. *p*-TTU	3080–3200*sb*	1610*s*	1250*m*	730*m*, 760*m*	1345*s*	1510*s*
D. *p*-TTU	3070–3200*sb*	1590*s*	1240*s*	750*m*	1400*s*	1450*s*
p-An. *p*-TTU	3260*m*	1620*m*	1260*s*	740*m*	1340*s*	1440*s*
β-Np. *p*-TTU	3300–3180*mb*	1600*s*	1270*w*	735*m*	1360*m*	1450*m*
DPTSCAZ	3420–3480*sb*	1580*s*	1250*s*	760*s*	1335*m*	1460–1470*sb*

s = strong; *w* = week; *m* = medium; *b* = broad

TABLE IV

IR spectral data of complexes and tentative assignments (cm^{-1})

COMPLEX	(N—H) Stretch	(N—H) Defore-mation	(C=S) Stretch	(CS+CN) stretch	(—NH—C=S) Stretch	(V=O) Stretch	(V—Cl) Stretch	(V—N) Stretch	(V—S) Stretch
$VOCl_3$.Bz.PTU	3120–3230*mb*	1480–1550*sb*	730–750*mb*	1310*m*	1445*mb*	1030*m*	370*w*	580–600*mb*	—
$VOCl_3$. *p*–ACNLD.PTU	3160–3350*sb*	1600*mb*	750*m*	1310*m*	1440*m*	—	320*w*	—	500*m*
$VOCl_3$.DPTU	—	1590*s*	760*s*	1360*m*	1430*s*	1020*w*, 1040*w*	310*w*	620*m*	500*w*, 530*w*
$VOCl_3$.*o*-T.PTU	3100*sb*	1590*s*	730*m*	1310*m*	1445*s*	1035*s*	—	590*w*	530*w*
$VOCl_3$.*p*-T.PTU	3160–3360*sb*	1600*s*	750*m*	1310*m*	1450*m*	1045*sb*	—	610*m*	—
$VOCl_3$.*m*-T.PTU	3160*s*	1615*s*	750*s*	1300*m*	1445*m*	1035*m*	370*w*	580*w*	520*w*
$VOCl_3$.*o*-An.PTU	3040–3570*sb*	1600*s*	755*mb*	1350*s*	1490*m*	—		610–630*m*	490–550*wb*
$VOCl_3$. *p*–An.PTU	4010–3200*mb*	1600*wb*	770*m*	1350*s*	1490*mb*	1040*s*	315*m*	570–600*wb*	520*w*
$VOCl_3$.*m*–An.PTU	3100–3180*mb*	1590*mb*	735*mb*	1340*mb*	1435*sb*	1020*m*	380*w*	600*w*	530*m*
$VOCl_2$.*o*–Pn.PTU	3145*m*	1620*s*	740*m*	1330*m*	1440*m*	1040*m*	—	—	510–530*mb*
$VOCl_3$. *p*–Pn.PTU	3135*m*	1630*s*	755*m*	1290*sb*	1480*mb*	1035*s*	310–340*wb*	590*m*	520*m*
$VOCl_3$.*m*–Pn.PTU	3100–3150*mb*	1630*s*	735*m*	1300*m*	1475*m*	1040*m*	305*w*	600*m*	535*m*
$VOCl_3$.α–Np.PTU	3140–3270*sb*	1580*s*	740*s*	1340*m*	1490*s*	1060*m*	300*w*	620*m*	530*m*
$VOCl_3$.β–Np.PTU	3185*mb*	1580*s*	740*s*	1340*m*	1470*s*	1060*w*	—	610*m*	530*m*
$VOCl_3$.Me.PTU	3130–3210*sb*	1530*m*	740–755*wb*	1310*w*	1485*mb*	1020*w*, 1040*w*		—	—
$VOCl_3$.Et.PTU	3090–3110*sb*	1540*m*	725*m*	1310*s*	1480*mb*	1040*s*	390*w*	580*w*	520*w*
$VOCl_3$P.*o*–TTU	3100–3130*mb*	1600*m*	740*m*	1320*s*	1430*sb*	1040*s*	335*w*	590*w*	—
$VOCl_3$.Bz *o*–TTU	3140–3260*sb*	1615*s*	735*sb*	1340*m*	1490*sb*	1030*w*	320*w*	570*m*, 600*m*	—

(*Continued*)

TABLE IV (*Continued*)

COMPLEX	(N—H) Stretch	(N—H) Deformation	(C=S) Stretch	(CS+CN) stretch	(—NH—C=S) Stretch	(V=O) Stretch	(V—Cl) Stretch	(V—N) Stretch	(V—S) Stretch
$VOCl_3$.D.*o*-TTU	3190–3230*mb*	1590*m*	720*s*	1320*mb*	1470*m*	1035*s*	360*w*	600*m*	—
$VOCl_3$.*p*-T.*o*-TTU	3105*sb*	1600*sb*	715*m*	1380*m*	1460*m*, 1510*s*	1020*w*, 1040*wb*	330*w*	—	530*w*
$VOCl_3$.*m*-T.*o*-TTU	3200*m*	1600*s*	760*s*	1370*s*	1485*s*	3035*s*	380*w*	610*w*	—
$VOCl_3$.*o*-An.*o*-TTU	3260–3390*sb*	1610*sb*	720*mb*	1300*m*	1510*s*	1025*mb*	—	570–590*wb*	510–530*wb*
$VOCl_3$.*p*-An.*o*-TTU	3210–3230*mb*	1605*mb*	710*sb*	1330*s*	1510*mb*	1040*m*	340*m*	590*w*	—
$VOCl_3$.*o*-Pn.*o*-TTU	3130–3150*sb*	1650*vw*	740*s*	1300*m*	1465*m*	1040*m*	310*w*	630*m*	—
$VOCl_3$.*p*-Pn.*o*-TTU	3230*s*	1640*s*	730*m*	1300*m*	1460*m*	1040*w*	300*w*	—	520*w*
$VOCl_3$.α-Np.*o*-TTU	3355*s*, 3110–3170*sb*	1600*s*	730*m*	1330*m*	1495*sb*	1040*w*	320–420*wb*	620*m*	530*w*
$VOCl_2$.P.*p*-TTU	3190*m*	1595*m*	745*m*	1310*m*	1440*m*	1020*w*	300–310*wb*	600*m*	510*m*
$VOCl_2$.Bz*p*-TTU	3280–3300*sb*	1585*m*	720*m*	1330*m*	1485*m*	1030*w*	295*w*	570*w*	530*w*
$VOCl_3$.D. *p*-TTU	3100–3120*mb*	1585*w*	710*m*	1390*m*	1455*m*	1040*s*	—	585*w*	—
$VOCl_3$.*p*-An.TTU	3200–3220*mb*	1605*s*	740*m*	1330*m*	1440*m*	1030*s*	—	—	530*w*
$VOCl_3$.β-Nn. *p*-TTU	3240*sb*	1620*m*	740*s*	1350*s*	1440*sb*	1060*m*	350*w*	600*m*	510
$VOCl_3$.DPTSCAZ	3120–3240*sb*	1580*w*	730–740*wb*	—	1400*mb*	1030*w*	—	600*m*	—

s=strong; *m*=medium; *b*=broad; *w*=weak

stretching vibrations[19]. In the complexes some new bands appear in the region 570–620, 510–530 and 300–390cm^{-1} which are assigned to ν(V-N), ν(V-S) and ν(V-Cl) modes rspectively.[20]

It is thus evident that ligands are bidentate and co-ordinated to the metal atom through thioketo sulphur and -NH nitrogen atoms. The six co-ordinated complexes [$(VOCl_3)$ (L)] so formed may have octahedral configuration involving d^2 Sp^3 hybridization.

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