

Vanadyl(V) chloride complexes of N-2 (4, 5, 6 monosubstituted pyridyl)-N'-substituted thio ureas

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Abstract. The complexing ability of vanadyl (V) chloride has been studied with N-2 (4, 5, 6 monosubstituted pyridyl)-N'-substituted thio urea ligands. The VOCl_3 has been observed to form the six coordinated, diamagnetic complexes of the type $\text{VOCl}_3 \cdot \text{L}$ where L is a bidentate ligand molecule. The ligands are co-ordinated to the vanadium metal through pyridyl nitrogen and thioketo sulphur atoms.

Keywords. Vanadyl (V) chloride complexes ; N-2 (4-methyl, 6-methyl, 5-nitro pyridyl)-N' (phenyl, ortho-tolyl, paratolyl, allyl) substituted thio ureas.

1. Introduction

Vanadium halides and oxyhalides are reported to form a number of complexes with mono, bi and polydentate ligands but very little is known about vanadyl (V) chloride complexes. VOCl_3 has been reported to form adducts of the type $\text{VOCl}_3 \cdot 2\text{L}$ (L = monodentate ligand) under mild conditions (Krauss and Gnatz 1962) but its reduction to VOCl_2 complexes is well-known (Paul and Kumar 1965). Reduction of VOCl_3 by aliphatic amines and thio ethers (Fowles 1964; Baker *et al* 1967) and carboxylic acids (Selbin 1965) with the formation of VOCl_2 complexes is also reported, however vanadyl(V) amino complexes with many primary, secondary and tertiary amines have also been prepared (Prasad and Upadhaya 1960). Literature revealed that no work has been done on complexing ability of VOCl_3 with bi or polydentate ligands. In this paper we report the isolation and characterization of vanadyl (V) chloride complexes with N-2 (4, 5, 6 monosubstituted pyridyl)-N'-substituted thio ureas.

2. Experimental

All the solvents and reagents used were guaranteed reagents. 2-amino pyridine, 2-amino-4-methyl, 2-amino-6-methyl and 2-amino-5-nitro pyridines were of

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Aldrich Chemicals. Allyl-iso-thiocyanate was of E Merck. Other mustard oils, viz., phenyl, *o*-tolyl and *p*-tolyl iso-thiocyanates were prepared (Vogel 1964) by reported procedures. All the solvents were purified by distillation after drying with appropriate reagent. Vanadyl (V) chloride was prepared (Prandtl and Bleyer 1909) by refluxing equimolar quantities of V_2O_5 and $SOCl_2$ over water bath for 6-8 hrs under rigorously anhydrous conditions. The product was distilled and the $VOCl_3$ fraction obtained at $125^\circ - 127^\circ C$ was dissolved in ether and analysed to check its purity (table 1).

The following ligands were prepared and characterized. The analytical results are as ligand (Abbreviated form); m.p. in $^\circ C$; % found S; (% calculated S); N-2 (Pyridyl)-N'-phenyl thio urea (Py · PTU); 169; 13.43 (13.93); N-2 (4-methyl pyridyl)-N'-phenyl thio urea (4 · MePy. PTU); 156; 12.79 (13.14); N-2 (6-methyl pyridyl)-N'-phenyl thio urea (6MePy. PTU); 180; 12.84 (13.14); N-2 (5-nitro pyridyl)-N'-phenyl thio urea (5NPy. PTU); 180; 12.47 (11.64); N-2 (pyridyl)-N'-ortho-tolyl thio urea (Py. *o*-TTU); 183; 12.67 (13.14); N-2 (4-methyl pyridyl)-N'-ortho-tolyl thio urea (4MePy. *o*-TTU); 192; 12.89 (12.43); N-2 (6-methyl, pyridyl)-N'-ortho-tolyl thio urea (6MePy. *o*-TTU); 161; 13.12 (12.43); N-2 (5-nitro pyridyl)-N'-ortho-tolyl thio urea (5NPy. *o*-TTU); 159; 11.51 (11.09); N-2 (pyridyl)-N'-paratolyl thio urea (Py. *p*-TTU); 182; 13.39 (13.14); N-2(4-methyl pyridyl)-N'-paratolyl thio urea (4MePy · *p*-TTU); 180; 11.99 (12.43); N-2 (6 methyl pyridyl)-N'-para-tolyl thio urea (6MePy. *p*-TTU); 153; 12.13 (12.43); N-2 (5-nitro pyridyl)-N'-para-tolyl thio urea (5NPy. *p*-TTU); 162; 11.21 (11.09); N-2 (pyridyl)-N'-allyl thio urea (Py. AlTU); 76; 16.48 (16.52); N-2 (4-methyl pyridyl)-N'-allyl thio urea (4MePy. AlTU); 103; 14.99 (15.41); N-2 (6-methyl pyridyl)-N'-allyl thio urea (6MePy. AlTU); 165; 14.93 (15.41); N-2 (5-nitro pyridyl)-N'-allyl thio urea (5NPy. AlTU); 158; 13.89 (13.41). All these were prepared by reported procedure (Krishnaswami and Bhargava 1969).

Ligands were characterized by their sharp melting points, elemental analysis and infra-red spectra.

All the operations in the preparation of complexes were carried out in a dry box. A requisite amount of ligand was dissolved in minimum quantity of chloroform and 0.02 M of solution was prepared by adding carbon tetrachloride. A 0.03 M CCl_4 solution of vanadyl (V) chloride was added drop by drop with constant stirring to an ice-cold ligand solution, maintaining in each case a slight excess of ligand. The mixture was frequently shaken and allowed to stand for 5 hr to attain equilibrium. The highly coloured complex was filtered and washed first with CCl_4 and then with little amounts of chloroform and ether in order to remove traces of unreacted ligand and $VOCl_3$ respectively. Synthesized complexes were dried in vacuum desiccator and analysed. After alkaline fusion the aqueous extract of weighed complex was divided into three parts to estimate vanadium volumetrically by titrating it against standard $KMnO_4$, sulphur as $BaSO_4$ and chloride as $AgCl$.

Magnetic measurements of the complexes were carried out on Gouy's balance using field strength of 5.0×10^3 Gauss and mercury tetrathiocyanato cobaltate as standard. Molar conductances were determined in N, N-dimethyl formamide (DMF) with conductivity meter type LBR of Wissenschaftlich technisch Werkenstatten, Germany using dip type cell. The infra-red spectra of ligands and

Table 1. Complexes of VOCl_3 with N-2 (4, 5, 6-monosubstituted pyridyl)-N'-substituted thioureas. Analytical data.

Compound	Colour	Melting point °C	Analysis of the compound					
			% Found			% Calculated		
			V	S	Cl	V	S	Cl
Vanadyl (V) chloride	Reddish yellow	..	29.52	..	62.13	29.39	..	61.36
VOCl_3 (Py, PTU)	Dark green	224	12.20	7.56	27.01	12.65	7.94	26.41
VOCl_3 (4MePy, PTU)	Dark green	142	12.65	7.89	26.09	12.22	7.68	25.52
VOCl_3 (6MePy, PTU)	Dark green	102	12.96	7.86	26.12	12.22	7.68	25.52
VOCl_3 (5NPy, PTU)	Yellowish green	162d	12.01	7.41	23.12	11.38	7.14	23.76
VOCl_3 (Py, o-TTU)	Dark green	210	12.10	7.93	25.84	12.22	7.68	25.52
VOCl_3 (4MePy, o-TTU)	Grey	145d	11.98	7.24	25.96	11.83	7.43	24.69
VOCl_3 (6MePy, o-TTU)	Green	182	11.54	7.19	24.97	11.83	7.43	24.69
VOCl_3 (5NPy, o-TTU)	Yellowish green	178	11.13	7.12	24.12	11.03	6.93	23.04
VOCl_3 (Py, p-TTU)	Green	92d	11.98	8.02	25.12	12.22	7.68	25.52
VOCl_3 (4MePy, p-TTU)	Yellowish green	115	12.23	7.98	24.94	11.83	7.43	24.69
VOCl_3 (6MePy, p-TTU)	Green	180	12.15	6.96	24.85	11.83	7.43	24.69
VOCl_3 (5NPy, p-TTU)	Light yellow	186	10.99	7.12	23.90	11.03	6.93	23.04
VOCl_3 (Py, AITU)	Green	124	12.98	8.14	29.48	13.89	8.72	29.01
VOCl_3 (4MePy, AITU)	Green	168	14.23	9.02	27.12	13.38	8.40	27.94
VOCl_3 (6MePy, AITU)	Green	182	13.87	8.48	26.98	13.38	8.40	27.94
VOCl_3 (5NPy, AITU)	Dark green	174	12.46	7.48	26.04	12.38	7.77	25.84

d = decompose

Table 2. IR spectral peaks of ligands and their VOCl_3 complexes (cm^{-1}).

Compound	$\nu(\text{NH})$	s (NH)	as (NH)	$\nu(\text{C}=\text{S})$	$\nu(\text{N}-\text{C}-\text{N}) +$ C=S	NH Rocking + $\nu(\text{NCN})$ + $\nu(\text{C}=\text{S})$	(C=C+C=N) stretch (in plane pyridyl ring defor- mation)	$\nu(\text{V}=\text{O})$	$\nu(\text{C}-\text{Cl})$
Py, PTU	..	1350m	1565s	765s	..	1478sb	1590sb
$[\text{VOCl}_3(\text{Py}, \text{PTU})]$..	1375wb	1550m	755mb	1310w	1460m	1590m	990sb	360w
4MePy, PTU	3212m	1364s	1550s	742w	1325s	1495s	1575m
$[\text{VOCl}_3(4\text{MePy}, \text{PTU})]$	3260s	1360m	1550s	710s, 750s	1315m	1450s	1580sb	985sb	310w
6MePy, PTU	3220m	1360m	1550s	750w	1325s	1435m	1580m
$[\text{VOCl}_3(6\text{MePy}, \text{PTU})]$	3260s	1360m	1550s	710s, 750s	1320m	1420w	1585sb	985sb	360w
5NPY, PTU	1572m	750vw	1325s	1470m	1590s
$[\text{VOCl}_3(5\text{NPY}, \text{PTU})]$	3240sb	1350s	1510m	750m	1320s	1420s	1615sb	990m	..
Py, o-TTU	3205-	1425s	1530s	725w	1335m	1470s	1570sb
$[\text{VOCl}_3(\text{Py}, o\text{-TTU})]$	3225mb	1350m	1550s	750s	1310m	1430s	1590sb	990s	730w
4MePy, o-TTU	3210-	1360s	1555sb	775w	..	1415m	1632s
$[\text{VOCl}_3(4\text{MePy}, p\text{-TTU})]$	3235mb	1350s	1540s	730s, 760m	1320m	1410s	1700w	1000sb	..
6MePy, o-TTU	3225mb	1382m	1550s	775m	1290w	1460s	1625s
$[\text{VOCl}_3(6\text{MePy}, o\text{-TTU})]$	3200mb	1350s	1545s	760m	1320m	1415sb	1690s	995sb	390vw
5NPY, o-TTU	3300-	1400sb	1560s	750s	1310s	1470m	159Cs
$[\text{VOCl}_3(5\text{NPY}, o\text{-TTU})]$	3365mb	1355s	1560m	740s	132Cs	1420w	1630s	980-1005wb	..
Py, p-TTU	3205-	1425s	1540s	760s	130Cs	1440m	1570sb
$[\text{VOCl}_3(\text{Py}, p\text{-TTU})]$	3225mb	1350m	1550s	750s	1310m	1420s	1580sb	980wb	380vw
5MePy, p-TTU	3260s	1390m	1555m	760w	1310m	1438w	1605s
$[\text{VOCl}_3(4\text{MePy}, p\text{-TTU})]$	3265mb	1340s	1550s	730s	1320m	1425m	1700w	985s	340m
6MePy, p-TTU	3260mb	1360s	1545s	770m	1310s	1445m	1590s

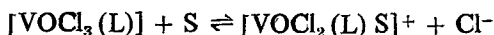
[VOCl ₃ (6MePy. <i>p</i> -TTU)]	3180sb	1350s	1560m	750m	1320s	1428w	1600s	..	365w
5 NPy. <i>p</i> -TTU	3300- 3365mb	1410wb	1570s	762wb	1325s	1470m	1570s
[VOCl ₃ (5NPy. <i>p</i> -TTU)]	3180sb	1360s	1560m	750s	1320s	1440s	1630s	990s	370-400wb
Py. AITU	3200- 3240mb	1410m	1535sb	775w	1325m	1445m	1590sb
[VOCl ₃ (Py. AITU)]	3170mb	1350m	1535s	730m, 770s	1310m	..	1620s	980sb	370-400wb
4MePy. AITU	3220m	1370s	1550sb	778w, 758w	1330s	1440w	1610w
[VOCl ₃ (4MePy. AITU)]	2920- 3300sb	1355mb	1530s	750s	1310m	1435s	1610mb	980sb	400mb
6MePy. AITU	..	1390m	1562mb	760m	1320m	1460sb	1615s
[VOCl ₃ (6MePy. AITU)]	2910- 3280sb	1350m	1560s	750s	1320s	1455sb	1620s	980sb	340wb
5NPy. AITU	3300	1400w	1570s	750s	1325s	1480m	1600s
[VOCl ₃ (5NPy. AITU)]	3360mb 3265sb	1350s	1570m	750s	1320s	1460m	1620s	..	370w

s = strong, w = weak, vw = very weak, m = medium, b = broad

complexes were determined using KBr pellet on infrared spectrophotometer of the type Beckman-20. The important peaks are recorded in table 2.

3. Results and discussion

Analytical results of the complexes correspond to the general empirical formula $\text{VOCl}_3 \cdot \text{L}$ where L is a ligand molecule (table 1). Molar conductance data of the complexes are in the range of $19.65\text{--}78.84 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which are well below those for typical 1 : 1 electrolyte ($85\text{--}135 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) (Suttons 1970; Sears *et al* 1955). It seems that partial replacement of chloride by solvent may be taking place as follows :



where S = solvent.

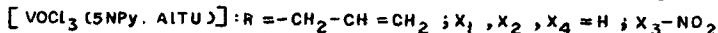
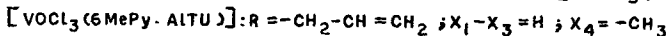
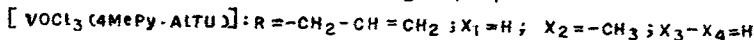
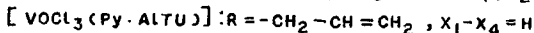
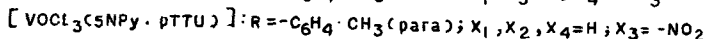
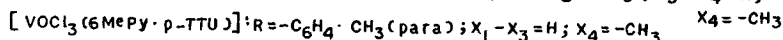
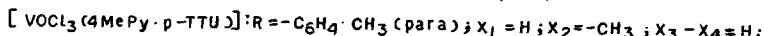
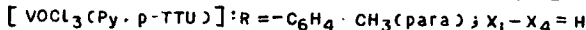
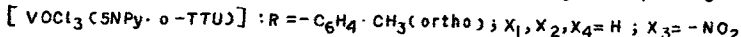
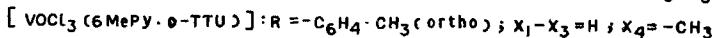
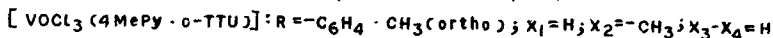
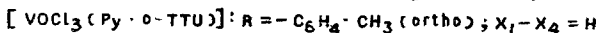
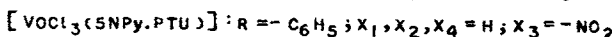
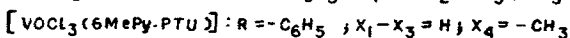
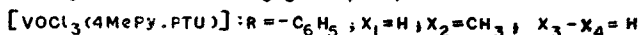
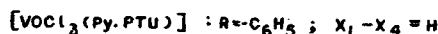
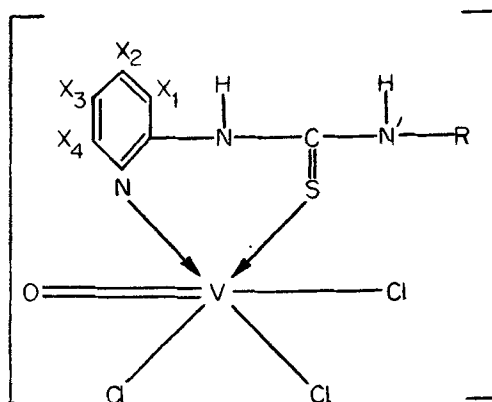


Figure 1. VOCl_3 complexes with N-2 (4,5,6 monosubstituted pyridyl)-N'-substituted thio-ureas.

All the complexes are diamagnetic as their magnetic susceptibility values are negative and in the range of -0.09 to -0.71×10^{-6} . The medium absorption bands appearing in the region $3200-3400 \text{ cm}^{-1}$ of the infra-red spectra of ligands have been assigned to the N-H stretching vibrations. There is very little change in these vibrations on complexation.

The bands appearing around 1320 cm^{-1} and 750 cm^{-1} in the ligand spectra have been ascribed to the ν (N-C-N⁺ C=S) and ν (C=S) vibrations respectively (Yamaguchi *et al* 1958). On complexation these bands are reduced in intensity and shifted down by $10-30 \text{ cm}^{-1}$. The sharp and medium absorption bands of the ligands appearing $\sim 1440 \text{ cm}^{-1}$ have been assigned to a combination of (NH) rocking and (C=S) and (N-C-N) stretching vibrations (Yamaguchi *et al* 1958). In the complexes these bands are lowered down by $10-35 \text{ cm}^{-1}$ with reduced intensity.

The bands around 1600 cm^{-1} in the ligands are due to the "in plane pyridyl ring deformation". These vibrations have been observed to be shifted to the higher frequency region by $20-30 \text{ cm}^{-1}$ in the complexes which shows that pyridyl ring nitrogen is co-ordinated to the vanadium metal atom (Banerjee and Singh 1968).

The spectra of VOCl_3 shows V=O stretch at 1035 cm^{-1} and $\nu\text{V-Cl}$ at 408 cm^{-1} which have been shifted to lower frequencies, 950 cm^{-1} and $310-400 \text{ cm}^{-1}$ in VOCl_3 complexes (McCormick and Jack 1968).

All these observations show that ligands are co-ordinated to the vanadium metal atom through thio keto sulphur and pyridyl ring nitrogen atoms.

VOCl_3 has been reported to have a distorted tetrahedral structure (Dijkgraaf 1965; Miller and Cousins 1957; Palmer 1938) which possibly has the d^2sp hybridization. It seems possible that the distorted tetrahedral symmetry of VOCl_3 has been changed to six co-ordinated irregular octahedral configuration with d^2sp^3 hybridization. On the basis of this information the complexes under investigation may be represented by the structure shown in figure 1.

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