

Synthesis of 1,5-disubstituted-2,4-dithiobiuret and 1,5-disubstituted-2-thiobiuret and their vanadyl (V) chloride complexes

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Abstract. Vanadyl (V) chloride forms $\text{VOCl}_3 \cdot \text{L}$ (L is a bidentate ligand molecule) type complexes with 1,5-disubstituted 2,4-dithiobiurets and 1,5-disubstituted-2-thiobiurets in carbon tetrachloride solution. Co-ordinations through sulphur atoms in case of 1,5-diaryl substituted 2,4-dithiobiurets and sulphur and oxygen in case of 1,5-diaryl substituted 2-thiobiurets have been proposed for these complexes.

Keywords. Vanadyl (V) chloride complexes ; 1,5-disubstituted 2,4-dithiobiurets ; 1,5-disubstituted-2-thiobiurets.

1. Introduction

Vanadyl(V) chloride forms $\text{VO}(\text{NHPh})_3$ type complex (Nelson and McFadden 1933) with aniline. Addition and substitution complexes of VOCl_3 are also known (Bunk *et al* 1958 ; Krauss and Gnatz 1962 ; Cozzi and Cecconi, 1953). Reduction of VOCl_3 by carboxylic acids, pyridine and aliphatic amines and thioethers with the formation of vanadyl (IV) carboxylates, $\text{VOCl}_2 \cdot 3 \text{C}_5\text{H}_5\text{N}$ and $\text{VOCl}_2 \cdot 2\text{L}$ where L is CH_3NH_2 ; $(\text{CH}_3)_2\text{S}$ and $(\text{C}_2\text{H}_5)_2\text{S}$ respectively is also reported (Selbin 1953 ; Paul and Kumar 1965 ; Baker *et al* 1967). Some unreduced $\text{VOCl}_3 \cdot 2\text{L}$ type VOCl_3 complexes with aromatic amines are also said to have been synthesized (Prasad and Upadhyaya 1960).

From the literature it has been found that no work has been carried out on complexing ability of VOCl_3 with polydentate ligands. We have synthesized the 1,5 disubstituted-2,4-dithiobiurets and 1,5-disubstituted-2-thiobiurets ligands and their VOCl_3 complexes.

2. Experimental

All the chemicals used were of either BDH "AnalaR" or MERCK GR grade. Solvents were purified by repeated distillation after appropriate drying. Phenyl isocyanate (mustard oil) used was of E. MERCK. Other mustard oils viz, phenyl, ortho-tolyl and para-tolyl isothiocyanate were prepared in the laboratory

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(Vogel 1962). Vanadyl (V) chloride was prepared (Hecht *et al* 1947; Prandtl and Bleyer 1909) by refluxing and distilling the mixture of V_2O_5 and $SOCl_2$. It was analysed to check its purity. Data are reported in table 1.

2.1. Synthesis of substituted dithiobiurets and thiobiurets ligands

The ligands 1,5-diphenyl 2,4-dithiobiuret (DPDTB); 1,5-diphenyl 2-thiobiuret (DPTB); 1-phenyl 5-paratolyl 2,4-dithiobiuret (P.p-TDTB); 1-phenyl 5-paratolyl-2-thiobiuret (P.p TTB); 1-orthotolyl-5-phenyl 2,4-dithiobiuret (*o*-TPDTB); 1-orthotolyl-5-phenyl-2-thiobiuret (*o*-TPTB); 1,5-diparatolyl 2,4-dithiobiuret (D-p-TDTB); 1,5-diorthotolyl 2,4-dithiobiuret (D-o-TDTB) and 1-methyl-5-paratolyl 2,4-dithiobiuret (Me-p-TDTB) were prepared by the known method (Dixit 1962). Purity of ligands was checked by their sharp melting points and elemental analysis (table 1).

2.2. Preparation of complexes

All operations were carried out in a dry box. The ligand was dissolved in minimum of chloroform and then 0.02 M solution was prepared by CCl_4 . $VOCl_3$ solution in CCl_4 (0.03 M) was added to the ice-cold ligand solution. The temperature of reaction mixture was kept below $10^\circ C$. The coloured complex was filtered, washed, dried and then analysed for vanadium, chloride and sulphur (Vogel 1959).

2.3. Instrumentation

The magnetic measurements of the complexes were carried out on Gouy balance. Molar conductance was determined in N,N-dimethyl formamide (10^{-3} M) on conductivity meter type LBR of Wissenschaftlich Technisch, Wersstatten, Germany, using a dip type cell. The IR spectras were taken on Perkins Elmer Grating infrared spectrophotometer model 237-B and 621. The important peaks of spectra are listed in table 2.

3. Results and discussion

Analytical results (table 1) correspond to the empirical formula $VOCl_3 \cdot L$, where L is a ligand molecule. The molar conductance values are in the range of 32.96-78.95 Mhos which are well below those for 1 : 1 electrolyte (Suttons 1971). The measured conductance values seem to be due to the partial replacement of chloride by solvent molecule. All the complexes are diamagnetic with a magnetic susceptibility $(-0.19 \text{ to } -0.43) \times 10^{-6}$.

In the ligands a medium broad band appearing around 3100-3200 may be due to the stretching of -NH group (Scheinmann 1970). On complexation these bands do not show any appreciable change. The bands in the region 1600 cm^{-1} in the ligands have been assigned to the -NH group deformation. Since these bands also do not indicate any change on complexation the possibility of nitrogen atom of thiourea -NH group as co-ordination site can be ruled out.

The C=S stretching vibrations in the ligands appear at $\sim 760 \text{ cm}^{-1}$ and 1250 cm^{-1} ; however both contain contribution from ν (CN) vibrations (Gosavi

Table 1. Colour, melting point and analytical data.

Substance	M.pt. °C	Colour	% found			% calculated		
			V	S	Cl	V	S	Cl
VOCl ₃	..	Reddish yellow	29.46	..	62.10	29.39	..	61.36
DPDTB	144	White	..	21.83	22.28	..
VOCl ₃ .DPDTB	96	Blackish green	10.93	13.21	22.01	11.06	13.89	23.09
DPTB	158	White	..	10.94	11.81	..
VOCl ₃ .DPTB	99	Light green	11.94	6.97	24.12	11.46	7.20	23.93
P. <i>p</i> -TDTB	123	Yellowish white	..	23.00	21.25	..
VOCl ₃ .P. <i>p</i> -TDTB	97	Green	11.14	13.02	23.12	10.73	13.48	22.41
P. <i>p</i> -TTB	189	Light yellow	..	11.53	11.22	..
VOCl ₃ .P. <i>p</i> -TTB	103	Bluish green	12.04	7.12	24.10	11.11	6.98	23.20
<i>o</i> -T.PDTB	118	Light yellow	..	22.01	21.25	..
VOCl ₃ . <i>o</i> -TPDTB	98	Yellowish green	10.93	13.58	23.02	10.73	13.48	22.41
<i>o</i> -T.PTB	174	Light green	10.94	11.22	..
VOCl ₃ . <i>o</i> -T.PTB	101	Light yellow	10.81	7.41	22.70	11.11	6.98	23.20
D. <i>p</i> -TDTB	142	White	..	21.46	20.30	..
VOCl ₃ .D. <i>p</i> -TDTB	93	Light yellow	9.84	14.02	22.10	10.43	13.10	21.77
D. <i>o</i> -TDTB	126	Yellowish white	..	21.14	20.30	..
VOCl ₃ .D. <i>o</i> -TDTB	94	Green	11.12	12.83	20.93	10.43	13.10	21.73
Me. <i>p</i> -TDTB	152	Light yellow	..	27.12	26.76	..
VOCl ₃ .Me. <i>p</i> -TDTB	103	Bluish green	13.01	16.12	27.01	12.35	15.51	25.78

Table 2. IR spectral data and tentative assignments (cm^{-1}).

Compound	(-NH) stretch	(C=O) stretch	(N-H) deformation	(C=S) stretch	Phenyl ring + (CN) stretch	(CS + CN) stretch	(NH) rocking + $\nu(\text{N}-\text{C}-\text{N}) + \nu(\text{C}=\text{S})$	(V=O) stretch
DPDTB	3120 m	..	1615 m	750 s	1535 s	1250 s	1480 m	..
VOCl_3 (DPDTB)	3125 m	..	1610 m	740 m	1550 b	1240 m	1470 vw	1020 m
DPTB	3230 s	1710 s	1600 vs	790 m	1500 vs	1227 s	1435 m	..
VOCl_3 (DPTB)	3220 mb	1700 m	1595 m	765 m	1510 m	1220 s	1430 m	1030 m
<i>P,p</i> -TDTB	3250 s	..	1600 s	750 w	1540 s	1260 mb	1465 m	..
VOCl_3 (<i>P,p</i> -TDTB)	3255 m	..	1605 m	740 m	1540 m	1245 m	1455 s	1025 mb
<i>P,p</i> -TTB	3196 w	1715 s	1620 s	785 w	1525 s	1295 m	1460 m	..
VOCl_3 (<i>P,p</i> -TTB)	3200 mb	1710 m	1625 s	765 mb	1530 m	1285 mb	1450 s	1030 m
<i>o</i> -T.PDTB	3235 m	..	1615 m	755 s	1570 m	1245 sb	1450 b	..
VOCl_3 (<i>o</i> -T.PDTB)	3230 mb	..	1635 m	740 mb	1575 w	1225 mb	1445 m	995 mb
<i>o</i> -T.PTB	3250 vs	1715 S	1620 vs	755 m	1540 m	1245 sb	1450 s	..
VOCl_3 (<i>o</i> -T.PTB)	3260 s	1695sb	1620 m	740 mb	1515 mb	1230 mb	1480 sb	975 mb
<i>D,p</i> -TDTB	3160 m	..	1625 m	795 s	1515 b	1155 m	1455 s	..
VOCl_3 (<i>D,p</i> -TDTB)	3150 m	..	1620 sw	740 wb	1510 w	1165 s	1440 mb	980 wb 1020 wb
<i>D,o</i> -TDTB	3215 m	..	162 s	750 s	1560 s	1260 m	1502 s	..
VOCl_3 (<i>D,o</i> -TDTB)	3210 mb	..	1635 s	740 s	1575 m	1245 s	1490 m	940 s 1040 m
<i>Me,p</i> -TDTB	3230 m	..	1610 m	755 m	1555 s	1255 m	1500 m	..
VOCl_3 (<i>Me,p</i> -TDTB)	3240 mb	..	1620 s	730 mb	1600 s	1205 wb	1480 s	1005 mb

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

et al 1967 ; Yamaguchi *et al* 1958). Both these bands on complexation are shifted down by 10-20 cm^{-1} with reduced intensity which indicates the possibility of thioketo sulphur atoms as co-ordination sites in complexes. The bands $\sim 1450 \text{ cm}^{-1}$ in ligands are assigned to the NH-C=S group vibration which is the combination of $\nu(\text{N-C-N})$, $\nu(\text{C=S})$ and $-\text{NH}$ rocking vibrations (Yamaguchi *et al* 1958 ; Randall 1949). The change in the nature of these vibrations on complexation further confirms the ligand co-ordination to the metal atom through thioketo sulphur atoms.

In DPTB, *P.p*-TTB and *o*-T-PTB ligands, the sharp peaks appearing around 1710 cm^{-1} have been assigned to the vibrations of $\nu(\text{C=O})$ group (Srivastava and Madhok 1978). On complexation the $\nu(\text{C=O})$ absorption peak shifts to a lower frequency by 10-20 cm^{-1} and becomes medium in intensity. The V=O stretching vibrations in the complexes appear $\sim 1030 \text{ cm}^{-1}$. These bands are weak and medium in intensity and are in the region expected for vanadium oxygen stretching frequencies (Miller and Cousins 1957).

All these observations show that co-ordination of DPDTB, *P.p*-TDTB, *o*-TPDTB, *D.p*-TDTB, *D.o*-TDTB and *Me.p*-TDTB ligands to the metal atom is through two thioketo sulphur atoms while in the case of DPTB, *P.p*-TTB and *o*-TPTB ligands it is through thio-keto sulphur and C=O group oxygen atoms. The six coordinated complexes $[\text{VOCl}_3(\text{L})]$ so formed may have octahedral configuration.

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