SYNTHESIS AND ELECTRICAL PROPERTIES OF VANADYL(V)CHLORIDE COMPLEXES OF N-2(4,5,6-MONOSUBSTITUTED PYRIDYL)-N'-ARYL SUBSTITUTED THIOUREAS

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Abstract—VOCl₃ formed six-coordinated complexes with N-aryl-N'-2(4,5,6-monosubstituted pyridyl)thioureas of the general formula [VOCl₃(RNHC—SNHR')], where R = pyridyl, 5-nitropyridyl, 4-methylpyridyl, 6-methylpyridyl groups and R' = $-C_6H_5$, o- C_6H_5 (CH₃) and p-C₆H₄(CH₃). The complexes have been characterized by means of elemental analysis, molar conductance, magnetic susceptibility, IR, UV–VIS, and ¹H NMR spectral data. The thermally stimulated depolarization effect was studied in samples polarized under different conditions. The results indicate two distinct transitions in the temperature range 92–100°C and 120–125°C for the ligands, whereas the VOCl₃-complexes show no breaks. The polarization–depolarization phenomena were correlated with the physicochemical changes occurring in the matrix. Depolarization kinetic data such as activation energy (E_a) and relaxation time (τ) of the electrets are reported.

Vanadium halides and oxyhalides are reported to form a number of complexes with mono, bi and polydentate ligands, but very little is known about the vanadyl(V)chloride complexes. Metal complexes of the substituted thioureas having heterocyclic group as one of the substituents have been studied by many workers.¹⁻³ Electrical properties of several metal Cu(II), Co(II), Ni(II) and Pt(II)phthalocynin complexes have been reported.4-5 Earlier communications⁶⁻¹⁴ have described the metal chelates of C=S, C=O and C=NH donor ligands. However, less work is available on the synthesis and physiochemical properties of VOCl₃ complexes with N-aryl-N'-2(4,5,6-monosubstituted pyridyl)thioureas. A literature survey reveals that a number of phase transitions have been reported in ferroelectric materials like substituted thioureas.15-19 Thus it was of interest to see what the electrical behaviour of such a ferroelectric substance will be, when incorporated in a complex matrix. The present study on VOCl₃-complexes with the title ligands was undertaken with the view to study the electrical changes.

EXPERIMENTAL

All the solvents and reagents used were guaranteed reagents. 2-aminopyridine, 2-amino-4-methyl, 2-amino-6-methyl and 2-amino-5-nitro pyridines were of Aldrich chemicals. The mustard oils like phenyl, orthotolyl, paratolyl-isothiocyanates were prepared by reported methods.²⁰ Vanadyl(V) chloride was prepared by refluxing equimolar quantities of V_2O_5 and SOCl₂ for 6–8 h and the product was distilled and the VOCl₃ fraction obtained at 125–127°C. The ligand *N*-aryl-*N'*-2(4,5,6-monosubstituted pyridyl)thioureas were prepared by the method reported earlier.¹³

GENERAL METHOD OF THE PREPARATION OF VOCl₃-COMPLEXES

All the operations in the preparation of metal complexes were carried out in a dry box. To a requisite amount of ligand (0.02 M) in CHCl₃/CCl₄ mixture was added 0.03 M CCl₄ solution of VOCl₃ drop by drop with constant stirring and was icecooled maintaining in each case a slight excess of the ligand. The mixture was shaken and allowed to stand for 8 h to attain equilibrium. The intensely coloured complexes were separated out, filtered washed with CCl₄ and CHCl₃. The complexes were analysed for V, S and Cl after fusion with alkali.

Magnetic measurements were carried out on a Gouy balance using a field strength of 5×10^3 Gauss

and mercury tetrathiocyanato cobaltate (II) as standard. Molar conductances were determined in N,Ndimethylformamide with conductivity meter type LBR of Wissenschaftlich technisch Werkenstatten, Germany using a dip-type cell. The IR spectra of the ligands and their metal-complexes were determined using KBr pellets on an infrared spectrophotometer of the type Beckman-20. Absorption spectra of VOCl₃ complexes were measured by standard methods using Perki–Elmer UV–VIS spectrophotometer model 139. Transition energy (E_T) was calculated by the relation

$$E_T = \frac{2.859 \times 10^5}{\lambda_{\max} (\text{in Å})}$$

and the oscillatory strength "f" was calculated from the equation

$$f = 4.32 \times 10^{-9} \int E_{\rm dv}$$

Utilizing

$$E_{\max}\Delta \bar{v} = \int E_{\mathrm{d}t}$$

where $\Delta \bar{v}$ is the wave number of the half band width.

All the electrical measurements were made on pellets pressed at a load of 9 tons at room temperature. The pellets were sandwiched between two aluminium electrodes. The capacitance was measured with a standard LCR bridge (Systronics 921) at 1 and 10 kHz as a function of temperature. The area A of the pellet was measured geometrically and graphically and the thickness d of the pellet was measured by a micrometer screw reading up to 0.001 cm. The dielectric constant ε was calculated from the equation

$$\varepsilon = C_0 d / (\varepsilon_0 A)$$

where $\varepsilon_0 = 8.85 \times 10^{-14} \text{ F cm}^{-1}$.

The sample was polarized at conditions $T_p = 90^{\circ}$ C, $E_p = 2.50 \times 10^3$ V cm⁻¹, $t_p = 2$ h. The heating rate was maintained at 6°C min⁻¹.

TSD spectra was recorded in the temperature range of 20 to 200°C. Activation energy, E_a was calculated by the initial rise method of Garlick and Gibson,²¹ from the slope of the straight line curve of log current (*i*) vs 1/T for the first lower half of the TSD peak.

$$\log i(T) = \text{constant} - \frac{E_a}{T}$$

where E_a = activation energy, T = absolute temperature and K = Boltzmann's constant.

Relaxation time of polarization created by ionic

motion or by dipoles orientation is given by the Arrhenius equation

$$\tau(T) = \tau_o \exp\left(-E_a/KT\right)$$

where $\tau(T)$ is the temperature dependent relaxation time of the dipoles in a dielectric, τ_o is the time constant and can be written as

$$E_o = \frac{kT_{\max}}{\beta E_a \exp\left(E_a/k\bar{T}_{\max}\right)}$$

where β = heating rate and T_{max} = peak temperature.

RESULTS AND DISCUSSIONS

All the VOCl₃ complexes are dark yellow–green coloured and soluble in chloroform, DMF, THF and nitrobenzene. All of them decompose above 225° C. The analytical results (Table 1) correspond to the general empirical formula VOCl₃·L where L is a bidentate ligand molecule. Since there is no loss of chlorine (wt%) in the complexes, reduction of V(V) to V(IV) may not be taking place. The electrolytic conductance measurements of these complexes (29–60 Ohm⁻¹ cm² mole⁻¹ in freshly distilled DMF solution indicate non-electrolytic nature of these complexes. The molar conductance of uniunivalent electrolytes are 80–90 mhos.²² It seems that partial replacement of chloride by solvent may be taken place as follows

$$[VOCl_3(L)] + S \rightleftharpoons [VOCl_2(L)S]^+ + Cl^-$$

where S is solvent. The magnetic susceptibility of the complexes were found in the range -0.043 to -0.71×10^{-6} G. The negative values of susceptibility indicate the diamagnetic nature of VOCl₃ complexes.

The electronic spectral bands of the complexes are listed in Table 2. All these bands are due to $M \leftarrow S$ charge-transfer absorption. Moor and Larsen²³ have earlier observed that $S \rightarrow M$ chargetransfer in xanthate complexes appears at 6000 cm⁻¹ below that of the corresponding dithiocarbamate complexes, and have suggested that xanthates are much greater reducing agents than dithiocarbamates. From the spectral data in our case, it is observed that the present ligands are not reducing agents.

The IR spectra of substituted thioureas and their VOCl₃ complexes are quite complicated, and therefore the effect of substitution could not be studied with a degree of certainty. The bands appearing at 3000–3400 cm⁻¹ have been assigned to $v_s(NH)$ and $v_{as}(NH)$, the latter being the higher frequency band. A medium broad band appearing at 3000–

			Analysis of the complexes					
		M	% found			% calculated		
Compound	Colour	м.р (°С)	v	S	Cl	v	S	Cl
VOCl ₃	Reddish		29.9		61.7	29.4		61.4
VOCl ₃ (PyPTU)	Green	225	12.4	7.9	26.4	12.6	7.9	26.4
VOCl ₃ (4MePyPTU)	Green	145	12.2	7.7	25.5	12.2	7.7	25.5
VOCl ₃ (6MePyPTU)	Green	120	12.2	7.5	25.5	12.2	7.7	25.5
VOCl ₃ (5NPyPTU)	Yellow	162d	11.4	7.1	23.7	11.4	7.1	23.8
$VOCl_3(5NPy \cdot oTTU)$	Yellow	178	11.0	6.9	23.0	11.0	6.9	23.0
VOCl ₃ (5NPy · pTTU)	Yellow	186d	11.0	6.8	22.9	11.0	6.9	23.0
VOCl ₃ (6MePy · oTTU)	Green	182	11.6	7.2	24.6	11.8	7.4	24.7
$VOCl_{3}(6MePy \cdot pTTU)$	Green	180	11.8	7.4	24.6	11.8	7.4	23.7
VOCl ₃ (Py · oTTU)	Green	215	12.0	7.7	25.5	12.2	7.7	25.5
VOCl ₃ (Py· <i>p</i> TTU)	Green	192d	12.1	7.6	25.0	12.2	7.7	25.5

	Table I	. Analy	tical data	l of V	OCl ₃	com	olexes
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d = decomposed.

3100 cm⁻¹ has been assigned to 2-aminopyridine vibrations. Bands appearing at 1600 and 1640 cm⁻¹ are assignable to v(C=C+C=N) modes of aryl groups. In the case of metal complexes there is a little change in this band. The bands appearing at 1132–1010 cm⁻¹ due to v(NCS+C=S) modes in the case of ligands are either reduced in intensity or

shifted to the higher frequency side in most of the complexes. The v(C=S) mode occurring at 750–775 cm⁻¹ in ligands is also shifted to the lower frequency side (20–25 cm⁻¹) in VOCl₃ complexes. The behaviour of the bands assigned to v(C=C+V=N) is of considerable importance in deciding whether or not the heterocyclic nitrogen is

Table 2	. Magnetic	susceptibility,	molar	conductance	and UV-	-VIS s	pectral d	ata of V	OCl ₃ -com	plexes
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		Molar	UV-spectral data in ethanol					
Complex	Magnetic susceptibility (×10 ⁻⁶)	$\begin{array}{c} \text{Motal} & = \\ \text{conductance,} \\ \Lambda_{M} \text{ cm}^{2} \\ \text{mole } \Omega^{-1} \end{array}$	λ _{max}	$\frac{E_{\max}}{(l \text{ mole}^{-1}/cm^{-1})}$	E_T (K cal/ mole)	"f"		
VOCl ₃ (PyPTU)	-0.302	29.8	275	24690	104.00	0.095		
			311	20950	91.91	0.085		
VOCl ₃ (4MePyPTU)	-0.430	40.2	278	16290	102.80	0.039		
			309	13920	92.51	0.032		
VOCl ₃ (6MePyPTU)	-0.420	50.50	281	25570	101.70	0.088		
			315	22870	90.76	0.067		
VOCl ₃ (5NPyPTU)	-0.717	52.20	276	18860	103.60	0.030		
			309	14110	92.51	0.142		
VOCl ₃ (5NPy · oTTU)	-0.420	56.20	276	28230	103.60	0.142		
			311	24100	91.91	0.136		
$VOCl_3(5NPy \cdot pTTU)$	-0.380	58.20	282	31090	101.40	0.127		
			314	26740	91.05	0.092		
VOCl ₃ (6MePy · oTTU)	-0.458	45.80	265	39320	107.90	0.722		
			318	34400	90.76	0.301		
VOCl ₃ (6MePy · <i>p</i> TTU)	-0.318	60.00	290	18740	105.90	0.170		
			308	18350	92.81	0.096		
VOCl ₃ (Py · oTTU)	-0.436	35.70	259	30950	110.40	0.334		
			308	28790	92.81	0.161		
$VOCl_3(Py \cdot pTTU)$	-0.471	38.80	264	30540	108.50	0.511		
			305	26130	93.74	0.170		

involved in the coordination with the metal ion. This band has been reported to be shifted to higher frequency in the case of coordinated pyridyl nitrogen.¹ In the present vanadyl(V)chloride complexes the band is increased by $10-30 \text{ cm}^{-1}$, which indicates that the ring nitrogen is also involved in the bond formation.

The frequency of the band assignable to V=O stretching mode in VOCl₃ is in agreement with the reported values.²³ (V=O stretch at 1035 cm⁻¹ and ν V-Cl at 408 cm⁻¹), which in the present case have been shifted to lower frequencies 950 cm⁻¹ (V=O) and 315-400 cm⁻¹ (V-Cl).

The ¹H NMR spectra of PyPTU, Py·oTTU, $P_{y} \cdot pTTU$ and 4MePyPTU indicate four distinct resonances: (i) a sharp singlet (δ 7.4–7.8 ppm) due to $-C_6H_5$ ring protons, (ii) a broad multiplet (δ 3.2–3.4 ppm) due to $o_{,p}$ -CH₃C₅H₄ ring protons, (iii) a sharp signal (δ 2.3–2.4 ppm) due to the protons of CH₃ groups and (iv) a doublet at (δ 4.35–4.42 ppm) due to NH protons of S=C---NH group. Finally a singlet at δ 8.4–8.6 ppm is possibly due to protons of the pyridyl ring. On account of poor solubility, the NMR spectra of VOCl₃ complexes with the above ligands were taken in deuterated DMSO. The spectra of V(V) complexes show the signal due to ---CNH group without any shift. The positions of the C_6H_5 and $o_{,p}$ -CH₃C₅H₄ ring protons remain unperturbed ruling out the possibility of coordination of ----NH group of NHC₆H₅. The lone pair of electrons on the nitrogen of the pyridyl ring causes a paramagnetic shielding of the 2- and 6protons.²⁴ Formation of the dative bonds using this electron pair greatly reduces the paramagnetic shielding giving a significant upfield shift for the

adjacent protons. In other words we can say that there is a decrease in the electron density of the pyridine ring upon complex formation. This decrease causes a reduction of the paramagnetic anisotropic effect. This will result in the almost uniform upfield shift for all the ring protons. In the VO(V)Cl₃ complexes of PyPTU, Py $\cdot oTTU$, Py $\cdot pTTU$ and 4MePyPTU, an upfield shift of heterocyclic ring protons by 3.0 to 4.8 ppm is observed confirming the coordination through pyridyl nitrogen.

All these observations show that ligands are coordinated to the vanadium metal though thio-keto sulphur and pyridyl ring nitrogen atoms.

VOCl₃ has been reported to have a distorted tetrahedral structure²⁵ which possibly has the d²sp hybridization. It seems possible that the distorted tetrahedral symmetry of VOCl₃ has been changed to six coordinated irregular octahedral configuration with d²sp³ hybridization. On the basis of the information, the complexes of VOCl₃ with the title ligands may be represented by Structure I.

ELECTRICAL PROPERTIES

Eley^{26,27} first observed the semiconducting properties of organic ligands and proposed that conductivity arose through thermal or optical excitation of electrons from the highest filled to the lowest empty orbital. The mechanism of conductivity is associated with the mobile electrons of the ligand rings. Earlier Day *et al.*²⁸ reported the resistivity of Fe-*p*H-thalocyanin as $4 \times 10^9 \Omega$ cm by a single crystal method. The present data on VOCl₃



For L PyPTU; 4MePyPTU; 6MePyPTU; 5NPy•oTTU; 5NPy•oTTU; 6MePy•oTTU; 6MePy•pTTU; 9MePy•pTTU; Py•pTTU; Py•oTTU;

 $\begin{array}{l} X_{1}, X_{2}, X_{3}, X_{4}, X_{5} = H \; ; \; W, X, Y, Z = H \\ X_{1} - X_{5} = H \; ; \; W = H \; ; \; X = CH_{3} \; ; \; Y = H \; ; \; Z = H \\ X_{1} - X_{5} = H \; ; \; Z = CH_{3} \; ; \; W = H \; ; \; X = H \; ; \; Y = H \\ Y = -NO_{2} \; ; \; W, X, Z = H \; ; \; X_{1} - X_{5} = H \\ Y = -NO_{2} \; ; \; W, X, Z = H \; ; \; X_{1} = CH_{3}, \; X_{2} - X_{5} = H \\ Y = -NO_{2} \; ; \; W, X, Z = H \; ; \; X_{3} = CH_{3}, \; X_{1} - X_{4}, X_{5} = H \\ Z = CH_{3}, \; W, X, Y = H \; ; \; X_{1} = CH_{3}, \; X_{2} - X_{5} = H \\ Z = CH_{3}, \; W, X, Y = H \; ; \; X_{3} = CH_{3}, \; X_{1}, X_{2}, X_{4}, X_{5} = H \\ W, X, Y, Z = H \; , \; X_{3} = CH_{3}, \; X_{1}, X_{2}, X_{4}, X_{5} = H \\ W, X, Y, Z = H \; , \; X_{1} = CH_{3}, \; X_{2} - X_{5} = H \\ W, X, Y, Z = H \; , \; X_{1} = CH_{3}, \; X_{2} - X_{5} = H \\ \end{array}$



Fig. 1. Current (i) vs 1/T for determination of activation energy (E_a) at T_{max} : \bigcirc , 138°C; \bigcirc , 130°C, \square . 122°C; for *o*-TP_yTU.

complexes is plotted as $\log \times \text{current}$ as a function of temperature in Fig. 1. At room temperature ρ is of the order of $4.7 \times 10^{11} \Omega$ cm and decreases with increasing temperature $(3.1 \times 10^{11} \Omega \text{ cm} \text{ at } 98^{\circ}\text{C})$. The log *i* vs 1/T plot is linear showing breaks at 92–100°C and 120–125°C for ligands. Activation energies, E_a have been calculated from the semilogarithmic plots of current (*i*) in the initial rise of the depolarization peak vs 1/T. The corresponding values of relaxation times were also calculated using Arrhenius equation from E_a values obtained in the initial rise method and are listed in Table 3.

As T_p increases, the t.s.d. peak shifts to higher temperatures. It is well known that, in homogeneous systems, polarization and depolarization phenomena are associated with dipoles and space charge effect, while the Maxwell-Wagner effect (interfacial polarization) becomes operative in a heterogeneous system. For example, in the presence of an air gap, heterogeneity is created giving rise to t.s.d. peaks. In the present study t.s.d. peaks were obtained from samples coated with aluminium as well as sandwiching them between aluminium electrodes. In both the cases similar types of t.s.d. peaks are obtained indicating the presence of no air gap in the samples, avoiding the possibility of interfacial polarization due to an air gap. Since the charging voltages are low (10^3 V cm^{-1}) , the homocharges by injection may not be present. Hence only polarization by dipole orientation and space charge effect are considered. Thus though the data taken together cannot conclusively establish the mechanism of depolarization, the trends are indicative of space-charge polarization. Beside physical effects, Stupp and Carr have shown that chemical changes can be associated with the t.s.d. peaks. In the present case heating will lead to further condensations, which would effect the t.s.d. peaks. Both the ligands and their VOCl₃ complexes show high dielectric constants. The dielectric constant of the ligands and complex are plotted as a function of temperature (Fig. 2). A broad shoulder is observed in the region 90-150°C in the PyPTU. On heating the dielectric constant of the complexes increases rapidly above 150°C, thus exhibiting the pyroelectric effect.

Thus, the electrical measurements along with the variations in IR spectral data, indicate the presence of two distinct transition temperature ranges $92-100^{\circ}$ C and $120-125^{\circ}$ C. It is proposed that up to $92-100^{\circ}$ C trapped water as well is present in the matrix. This is reflected in a decrease in resistivity.³⁰ On continuous heating chain mobility is increased. Thus it is proposed that the t.s.d. peaks at $92-100^{\circ}$ C

	F	T	$ au_{T_{\max}}$			
Compound	(eV)	I_{max} (°C)	(S)	(day)		
o-TPyTU	0.52	122	4.05×10^{2}	0.00468		
	0.73	130	2.93×10^{2}	0.00339		
	1.16	138	1.91×10^{2}	0.00221		
VOCl ₃ ·o-TP _y TU	0.39	122	5.20×10^{2}	0.00680		
	0.89	138	2.315×10^{2}	0.00303		

Table 3. Activation energies (E_a) and depolarization kinetic data obtained for o-TP_vTU and VOCl₃·o-TP_vTU

 E_a is activation energy.

 $T_{\rm max}$ is temperature of the t.s.d. peak.

 $\tau_{T_{\text{max}}}$ is the relaxation time at T_{max} .



Fig. 2. Plot of Dielectric Constant versus temperature at 1 and 10 kHz.

are due to a physical effect associated with trapped water and the one at $120-125^{\circ}C$ is attributed to both physical and chemical transitions.

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