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NATURE OF CHLOROPHENOXY DERIVATIVES OF NIOBIUM (V)

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ABSTRACT

Compounds of composition $NbCl_n(OC_6H_4Cl)_{5-n}$, $n = 0 \rightarrow 4$, have been prepared by reacting niobium (V) chloride with O-chlorophenol in predetermined molar ratios in carbon tetrachloride. Based upon elemental analysis, conductance, infrared, magnetic and thermogravimetric analysis, their structures have been proposed.

INTRODUCTION

MALHOTRA and Martin[1] have recently reviewed physico-chemical properties and uses of metal phenoxides. A number of *bis* (substituted phenoxo) titanium (IV) complexes have been prepared and characterised by Harrord and Taylor[2]. Though compounds of composition $VCl_2(OC_6H_4Cl)_2$ and $VCl_2(OC_6H_4NO_2)$ with O-chloro and nitrophenol respectively have been isolated, the product obtained from VCl_4-phenol mixture has not been well characterised[3]. A series of *bis* (aryloxo) iron (II) complexes of the type $Fe(OC_6H_4X)_2.(bipy)_n$ have also been prepared and characterised[4]. In the present studies we report the synthesis of chlorophenoxy derivatives of niobium (V) and propose a possible structure on the basis of elemental analysis, molar conductance, TGA and magnetic and infrared spectral studies.

EXPERIMENTAL

O-Chlorophenol (AR) was purified by distillation under reduced pressure. Niobium pentachloride was of Fluka, analytical grade and was used as such without further purification. The organic solvents used were of AnalaR grade and were dried by appropriate drying agents, distilled and finally preserved over activated molecular sieves.

Compounds of composition $NbCl_4(OC_6H_4Cl)$ and $NbCl_3(OC_6H_4Cl)_2$ were obtained by stirring a suspension of niobium pentachloride with O-chlorophenol

in 1:1 and 1:2 molar ratio in carbon tetrachloride till there was no evolution of hydrogen chloride gas. But in the case of compounds of composition $NbCl_2(OC_6H_4Cl)_3$, $NbCl(OC_6H_4Cl)_4$ and Nb-$(OC_6H_4Cl)_5$, the components mixed in predetermined molar ratios had to be refluxed till evolution of hydrogen chloride gas ceased. The compounds were isolated as solids by the addition of petroleum ether to the resulting coloured solutions, filtered, washed repeatedly with carbon tetrachloride and dried under vacuum.

Niobium was estimated as its pentoxide and chlorine by Volhard's method. Infrared spectrum of the compounds was recorded on a double grating infrared spectrophotometer Perkin Elmer 337 and 621 in KBr pellets. Molar conductances of 10^{-3} M solution of these compounds in nitrobenzene were measured using a cell (cell constant 0.334) at $25 \pm 0.1°C$ with a Toshniwal conductivity bridge CL01/01A Sl. No. 447. Magnetic measurements were made on a Guoy balance at room temperature. Thermal analysis was carried out on a Stanton thermogravimetric balance, model AD-2 at a heating rate of 5°/min.

RESULTS AND DISCUSSION

The compounds which have been isolated in the present studies are $Nb(OC_6H_4Cl)_5$, dark yellow m.p. 94°C; $NbCl(OC_6H_4Cl)_4$, yellow, m.p. 210°C; $NbCl_2(OC_6H_4Cl)_3$, light red, 140°C; $NbCl_3$ $(OC_6H_4Cl)_2$, red, 62°C and $NbCl_4(OC_6H_4Cl)$, red, 118°C, their stoichiometric composition being established by the analysis of niobium and chlorine

which agreed with the calculated values within the limits of experimental errors. They are quite moisture-sensitive and change their colours on exposure but are sufficiently stable in dry atmosphere. They are insoluble in benzene, nitromethane, acetonitrile, dioxane but are fairly soluble in nitrobenzene and dimethylformamide. Molar conductance values of millimolar solutions $(10^{-3}$ M) of these compounds in nitrobenzene are in the range $0.87-1.89$ ohm^{-1} cm^2 mole^{-1} which are very low as compared to values reported for 1:1 electrolytes[5] and thus suggest that they are non-electrolytes. Molecular weight determinations of these compounds could not be carried out because of their insolubility in solvents suitable for cryoscopy. These compounds have been diamagnetic and therefore excludes the possibility of any reduction of the metal to the lower oxidation state.
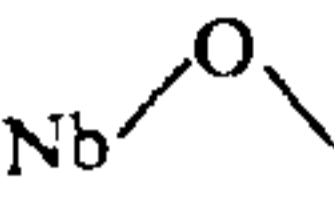
Information on the structure of these compounds has been derived from the significant change in the spectrum of pure O-chlorophenol on compound formation. The broad band observed in the region $3350-3480$ cm^{-1}, due to hydrogen bonded phenolic group[6,7] in pure phenol is missing in its compounds which is also supported by the observation that hydrogen chloride gas is evolved during the course of reaction. All important bands are given in table 1 and it is evident that changes in various bands are similar to those observed for various aromatic tertiary bases upon complexation with metal and non-metal halides[8,9]. The most important and strong band present at ~1250 cm^{-1} in pure ligand assigned to $v(O-C)$ stretching modes has been lowered by about $60-70$ cm^{-1} suggesting a considerable contribution
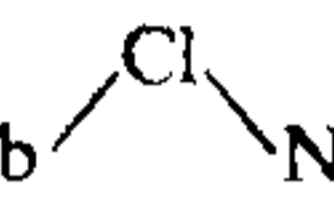
Table 1 *Principal IR spectra bands (cm^{-1}) of chlorophenoxides of niobium (V).*

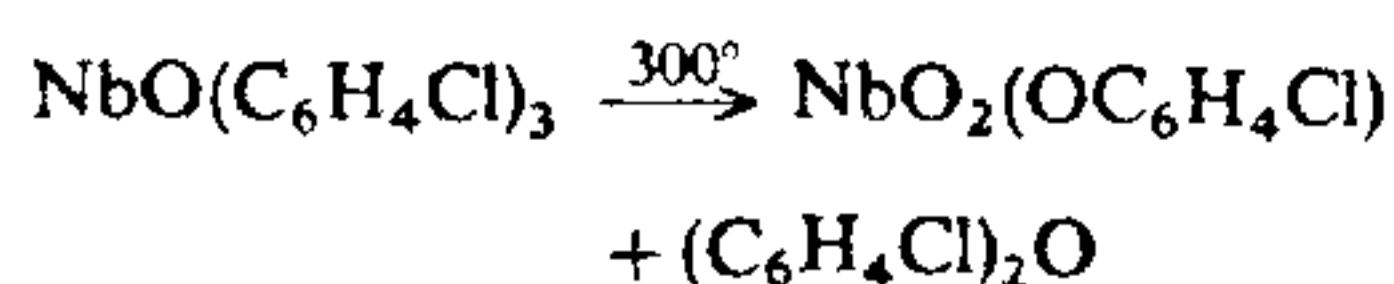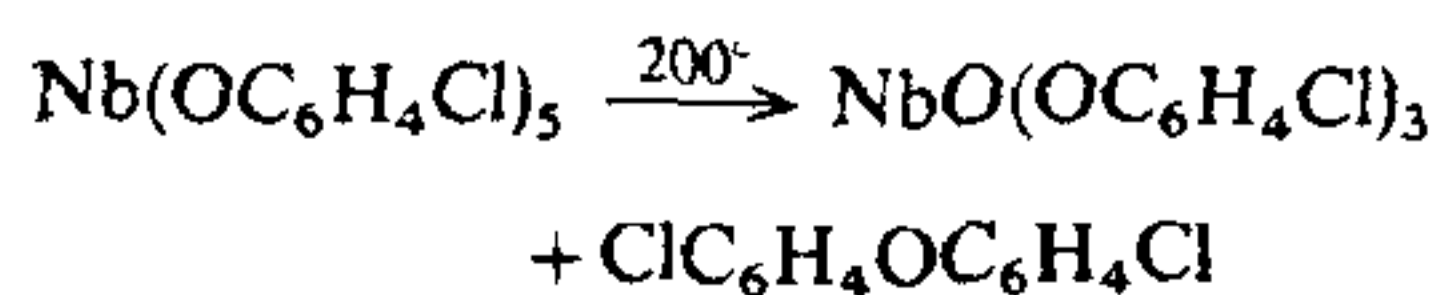| ClC$_6$H$_4$OH	Nb(OC$_6$H$_4$Cl)$_5$	NbCl(OC$_6$H$_4$Cl)$_4$	NbCl$_2$(OC$_6$H$_4$Cl)$_3$	NbCl$_3$(OC$_6$H$_4$Cl)$_2$	NbCl$_4$(OC$_6$H$_4$Cl)	Assignment
3480,3390	—	—	—	—	—	v(OH)
3070,3052	3072,3048	3074,3045	3078,3046	3074,3048	3072,3050	$v(=CH)$
3020	3018	3018	3022	3020	3018	
1620,1590	1635,1595	1628,1592	1625,1592	1624,1590	1620,1595	$v(C=C)$
1480,1422	1482,1428	1485,1426	1482,1425	1480,1420	1483,1421	
1358,1338	—	—	—	—	—	v(ring) + δ(OH)
1250	1210,1188	1208,1190	1206,1185	1200,1188	1201,1185	$v(O-C)$
1160,1152	1165,1120	1162,1102	1170,1152	1160,1148	1162,1450	β(CH)
1078,1020	1080,1022	1072,1024	1085,1032	1078,1028	1072,1025	
972, 950	970,945	978, 965	976, 962	972, 958	975, 952	v(CH)
870, 820	875, 820	870, 825	868, 815	860, 812	864, 810	
788, 702	780, 700	785, 710	782, 706	780, 702	786, 698	Inplane def
620, 598		608	602	600	605	bands of ring
	576	572	580	578		v(Nb-O)
	528	532	532	526	528	(Nb$\diagup$O$\diagdown$Nb)
		352	350	352	358	
				348	352	v(Nb-Cl)

from a structure of the type $M^- - O^+ = C$. Similar explanation has been advanced by Bradley and coworkers in the case of metal alkoxides.

Coordination from oxygen of the ligand to niobium has been further confirmed by the appearance of entirely new bands (not present in the ligand) in the lower spectral region. While intense bands in the region 578–580 cm^{-1} may be assigned to IR active terminal $v(Nb-O)$ stretching modes, the bands at 530–540 cm^{-1} are attributed to the bridging

Nb$\overset{O}{\diagdown}$Nb modes because bridging modes are expected to absorb at lower spectral regions than those of terminal modes[10-12]. It is interesting that no band around 900–930 cm^{-1} which could be assigned to Nb =O stretching modes has been observed in these compounds which suggests that no oxygen abstraction occurs in these compounds[13,14]. Furthermore, sharp intense bands in the region 340–350 cm^{-1}, assigned to $v(Nb-Cl)$ stretching modes, are also observed which agree with the assignments of Djordjevic[15] and with the reported $v(Nb-Cl)$ vibrations for octahedral complexes[16]. No band that could be assigned to

bridging Nb$\overset{Cl}{\diagdown}$Nb modes expected to fall well below 300 cm^{-1} has been observed[17]. Based upon elemental analysis, conductance, IR spectral data and insolubility in various solvents, a possible dimeric structure bridging through chlorophenoxy groups may be proposed. These propositions also find support from previous work on the alkoxides and phenoxides of niobium and tantalum[18-20].

The relative strength of bonds in the chlorophenoxides and possible thermal mode of decomposition has been inferred from the weight changes as noted from thermograms. Although the final product in all these phenoxides in Nb_2O_5, it is difficult to comment precisely as to what type of intermediates are formed *e.g.* in the case of compounds of composition $NbCl_3(OC_6H_4Cl)_2$, a molecule of dichlorobenzene is lost at about 200°C leaving behind niobium oxytrichloride, which decomposes further *via* niobium dioxymonochloride (NbO_2Cl) formation at ~ 300°C followed by subsequent disproportionation to the pentoxide[21] at about 650°C. However, in the case of fully substituted $Nb(OC_6H_4Cl)_5$, the major intermediate products are chlorophenyl ether and niobium oxytrichlorophenoxide as follows:

$$Nb(OC_6H_4Cl)_5 \xrightarrow{200°} NbO(OC_6H_4Cl)_3$$

$$+ ClC_6H_4OC_6H_4Cl$$

$$NbO(C_6H_4Cl)_3 \xrightarrow{300°} NbO_2(OC_6H_4Cl)$$

$$+ (C_6H_4Cl)_2O$$

$$NbO_2(C_6H_4Cl) \xrightarrow[Air]{650°} Nb_2O_5 + (C_6H_4Cl)_2O.$$

Formation of these intermediates is supported by the earlier reports[22,23] on the decomposition trends of alkali metal and transition metal phenoxides[18]. It can thus be concluded that these chlorophenoxides have sufficient thermal stability due to their polymeric nature.

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ALTERATIONS IN STRUCTURE AND FUNCTION OF ADRENAL GLAND DUE TO BILATERAL VAGOTOMY IN DOMESTIC PIGEONS

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ABSTRACT

Histomorphological studies carried out on adrenal glands of bilaterally vagotomized pigeons showed that adrenals, to some extent, are dependent on vagal nerve for structural and functional integrity. Vagotomy resulted in an increase of adrenal weights. This increase was seen in both absolute and relative weights of the gland. Histochemical preparations revealed a hypertrophy of cortical tissue and a regression of medullary tissue. Activity of acetylcholinesterase as well as ascorbic acid content showed a decrease in the adrenal gland of vagotomized pigeons. However, there was an increased accumulation of lipid droplets in the cortical cells. The results indicate that in pigeons, the vagal transection leads to cortical hypertrophy but a slight reduction in steroidogenic activities.

INTRODUCTION

ADRENOCORTICOSTEROIDS and catecholamines secreted by adrenal gland are involved in metabolic, thermoregulatory, reproductive and many other physiological changes taking place in birds[1,2]. Some of these are long term changes and hence seasonal or related to environmental conditions. Several adrenal functions are related to short term regulation and are mostly metabolic. While long term regulations are mediated by hormones such as ACTH[1], the short-term regulations are modulated by autonomous nervous sytem.

In mammals, the nerves of both parasympathetic and sympathetic systems have regulatory influence on the adrenal. Subdiaphragmatic splanchnotomy in male rats resulted in a reduction of catecholamine content of adrenal medullary cells[3] and an activation of adrenal cortical cells[4], indicating that sympathetic nerves have an inhibitory effect on cortical cells and stimulatory effect on medullary cells. On the other hand bilateral subdiaphragmatic vagotomy resulted in a decrease in functional activities of adrenal cortical cells[5-8]. Avian adrenal gland is different from mammalian adrenal by the absence of zonation of cortical and medullary cells, although both splanchnic and vagal innervations are same as in mammals[9]. However, the functional relationship between autonomous nerve fibres and adrenal activity has not been clearly established in birds as in mammals. In the present report, an attempt to understand the influence of vagal fibres on the adrenal gland is made by subjecting pigeons to bilateral vagotomy.

MATERIALS AND METHODS

Adult domestic pigeons (*Columba livia*) of both sexes weighing 250 to 300 g and acclimated to laboratory conditions were used in the experiments. The birds were divided into four groups of five birds each. Two groups of pigeons, injected with sodium phenobarbitone (40 mg/kg body weight) as anaesthetic agent, were bilaterally vagotomized from cervical region and