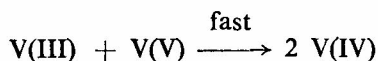
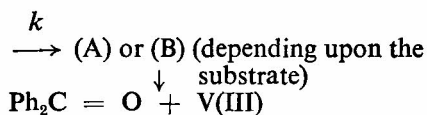
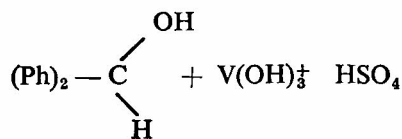
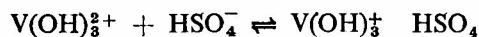


TABLE 2 — THERMODYNAMIC PARAMETERS FOR VARIOUS SUBSTITUENTS IN V(V)—BENZHYDROL REACTION IN SULPHURIC ACID MEDIUM

Substituent	k_2 (at 55°C) (litre mol ⁻¹ sec ⁻¹)	ΔE_a^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ deg ⁻¹	σ^*
— H	11.4×10^{-3}	64.37	—104.5	0.0
4-NO ₂	3.5×10^{-2}	39.29	—175.56	+0.779
4-Me	0.99×10^{-2}	66.28	—179.74	—0.17
4-4'-di-Cl	2.9×10^{-2}	38.99	—175.56	+0.454
4-4'-di-Me	2.5×10^{-2}	55.59	—158.84	—0.34
4-4'-di-OMe	3.95×10^{-1}	76.49	— 37.62	—0.536

*Values taken from *Physical organic chemistry* (McGraw-Hill, New York), by Jack Hine (pp. 87). Values for disubstituted compounds have been evaluated using the vector sum of individual substituent constants.

results obtained, the following mechanism is proposed:—



Scheme 1

No polymerisation of acrylonitrile is observed indicating that the free radicals are not produced. If at all free radicals are produced they react faster with oxidant than with acrylonitrile.

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Chlorotitanium(IV) Derivatives of Salicylaldehyde Hydrazone & o-Hydroxyacetophenone Hydrazone, & Their Addition Compounds with Nitrogen Bases†

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Hydrazones of salicylaldehyde and o-hydroxyacetophenone (HR-N-NH₂) react with TiCl₄ to give trichloro- and dichloro-titanium derivatives, (R-N-NH₂)TiCl₃ and (R-N-NH₂)₂TiCl₂. The trichloro-titanium compounds furnish stable 1:1 adducts with pyridine, quinoline, 2,2'-bipyridyl, pyridine N-oxide, 1,10-phenanthroline and tri-n-octylphosphine oxide. Similar adducts of salicylaldehydotrichlorotitanium with these donor ligands have also been prepared. In these addition compounds the titanium atom appears to be hexacoordinated.

SINN and Harris¹ have reviewed the interesting chemistry of complexes with N-N grouping. Recently Tandon *et al.*² have synthesized salicylaldehyde-, o-hydroxyacetophenone- and naphthaldehyde-complexes of boron. Aggarwal *et al.*³ have studied transition metal complexes of salicylaldehyde hydrazone. New organotin and organoxytitanium derivatives of salicylidene salicylhydrazide were reported from this laboratory⁴. Trichloro- and dichloro-titanium derivatives of salicylaldehyde hydrazone and o-hydroxyacetophenone hydrazone and the addition compounds of the trichlorides with several nitrogen bases are reported in this note along with adducts of salicylaldehydotrichlorotitanium. Hydrazones of salicylaldehyde and o-hydroxyacetophenone were prepared as described by Aggarwal *et al.*³ Properly dried solvents were used and all experiments were conducted in dry atmosphere.

Trichloro- and dichloro-titanium derivatives of salicylaldehyde hydrazone and o-hydroxyacetophenone hydrazone—Freshly distilled (over Cu turnings) titanium tetrachloride (9.5 g; 0.05 mol) was diluted with benzene (25 ml) and cooled in ice. To this was added a solution of salicylaldehyde hydrazone

†NCL Communication No. 2732.

(6.8 g; 0.05 mol) in the same solvent (25 ml) dropwise with constant stirring. The mixture was gently refluxed for 2 hr and the brown solid obtained was filtered, washed with benzene-methanol (95:5, v/v), and hexane and dried *in vacuo* at 60°; yield quantitative. The compound was soluble only in ethyl alcohol, m.p. 200° (d). (Found : Ti, 15.60; Cl, 34.24. $C_7H_7ON_2TiCl_3$ requires Ti, 15.50; Cl, 34.13%).

o-Hydroxyacetophenonehydrazonetrichlorotitanium and salicylaldehydotrichlorotitanium were prepared similarly. The dichloro compounds of hydrazones were obtained when the ligand (2 mol) and $TiCl_4$ (1 mol) were allowed to react as above. All of them were insoluble in common organic solvents and melted above 200°. Analysis : (i) *o*-hydroxyacetophenonehydrazonetrichlorotitanium. (Found : Ti, 15.74; Cl, 30.00. $C_8H_{10}ON_2TiCl_3$ requires Ti, 15.81; Cl, 30.43%). (ii) *bis*:*o*-hydroxyacetophenonehydrazonodichlorotitanium — (Found : Ti, 11.72; Cl, 16.96. $(C_8H_9ON_2)_2TiCl_2$ requires Ti, 11.49; Cl, 17.01%) and (iii) *bis*-salicylaldehydohydrazono dichlorotitanium — (Found : Ti, 12.17; Cl, 18.40. $(C_7H_7ON_2)_2TiCl_2$ requires Ti, 12.31; Cl, 18.23%).

Addition compound with quinoline — A solution of freshly distilled quinoline (0.65 g; 0.005 mol) in benzene (10 ml) was added to a suspension of salicylaldehydotrichlorotitanium (1.38 g; 0.005 mol) in the same solvent (15 ml). A colour change took place and the contents were stirred at room temperature for 2 hr. The insoluble adduct was separated, washed with benzene-methanol (95:5 v/v) and hexane and dried at room temperature *in vacuo*; yield 80% (1.6 g). Other addition compounds were prepared similarly (Table 1).

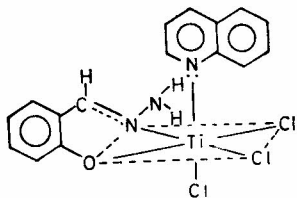
The trichlorotitanium compounds were brown and the addition products were all yellow solids, highly hygroscopic, decomposing in moist air. They were insoluble in common solvents like benzene and CCl_4 , but soluble in ethyl alcohol. All of them decomposed on heating above 200°; the salicylaldehydotrichlorotitanium adducts were stabler than the rest. Because of their insolubility, the PMR spectra and molecular weight could not be recorded. The adducts formed from the dichlorotitaniums were much less stable and less characterised.

The IR spectrum of salicylaldehyde hydrazone exhibited following characteristic bands : 3370 (ν_{as} NH), 3260 (ν_s NH), 3050-2900 [ν O-H (phenolic) + ν CH], 1620 (ν C=N); 1260 [ν C-O (phenolic)] and 940 cm^{-1} (ν N-N). In the IR spectra of mono- and di-substituted derivatives of this ligand with $TiCl_4$ there was a downward shift of ν_{as} NH (3210), ν_s NH (3180) and ν C=N (1590, 1600). The ν C-O (phenolic) had undergone an upward shift to 1280 and ν N-N was split and seen at 985, 975 and 905. All these spectral behaviour indicates a strong chelation with proton replacement by titanium atom³.

The IR spectrum of *o*-hydroxyacetophenone hydrazone exhibited characteristic bands at 3390, 3295, 3210 (ν NH)⁵, 1625 (ν C=N), 1285 [ν C-O (phenolic)] and 930 cm^{-1} (ν N-N). In the IR spectra of trichloro- and di-chlorotitanium derivatives, formed by proton replacement, the above absorption bands underwent considerable shift. The ν NH were observed at 3320 and 3240, ν C=N at 1585, ν C-O (phenolic) at 1315 and ν N-N at 970. Hence like the salicylaldehyde hydrazone derivative, these compounds also exist as a strongly chelated molecule. In mono- and bis-salicylaldehydohydrochlorotitaniums, the

TABLE 1 — ADDITION COMPOUNDS OF CHELATED TRICHLOROTITANIUMS

Donor molecule	Product	Found (Calc.) (%)	
		Ti	Cl
A. Salicylaldehydotrichlorotitanium(IV)			
1. Pyridine	$LTiCl_3 \cdot C_5H_5N$	13.83(13.52)	29.87(30.04)
2. Quinoline	$LTiCl_3 \cdot C_9H_7N$	11.96(11.85)	26.13(26.29)
3. 2,2'-Bipyridyl	$LTiCl_3 \cdot C_{10}H_8N_2$	11.34(11.10)	24.35(24.67)
4. Pyridine N-oxide	$LTiCl_3 \cdot C_5H_5NO$	12.81(12.97)	28.59(28.71)
5. 1,10-Phenanthroline	$LTiCl_3 \cdot C_{12}H_8N_2$	10.90(10.52)	23.12(23.35)
6. Tri- <i>n</i> -octylphosphine oxide	$LTiCl_3 \cdot C_{24}H_{51}PO$	7.98(7.24)	15.89(16.06)
B. Salicylaldehyde hydrazonotrighlorotitanium(IV)			
1. Pyridine	$LTiCl_2 \cdot C_5H_5N$	12.85(13.00)	28.44(28.89)
2. Quinoline	$LTiCl_2 \cdot C_9H_7N$	11.01(11.45)	25.01(25.44)
3. 2,2'-Bipyridyl	$LTiCl_2 \cdot C_{10}H_8N_2$	10.36(10.75)	23.46(23.89)
4. Pyridine N-oxide	$LTiCl_2 \cdot C_5H_5NO$	11.92(12.48)	27.15(27.66)
5. 1,10-Phenanthroline	$LTiCl_2 \cdot C_{12}H_8N_2$	10.09(10.22)	22.77(22.68)
6. Tri- <i>n</i> -octylphosphine oxide	$LTiCl_2 \cdot C_{24}H_{51}PO$	7.11(7.10)	15.47(15.74)
C. <i>o</i>-Hydroxyacetophenone hydrazonotrighlorotitanium(IV)			
1. Pyridine	$LTiCl_2 \cdot C_5H_5N$	12.35(12.89)	28.05(28.54)
2. Quinoline	$LTiCl_2 \cdot C_9H_7N$	10.97(10.37)	24.96(25.20)
3. 2,2'-Bipyridyl	$LTiCl_2 \cdot C_{10}H_8N_2$	10.55(10.68)	23.86(23.67)
4. Pyridine N-oxide	$LTiCl_2 \cdot C_5H_5NO$	12.78(12.36)	27.59(27.96)
5. 1,10-Phenanthroline	$LTiCl_2 \cdot C_{12}H_8N_2$	10.10(9.91)	22.01(21.98)
6. Tri- <i>n</i> -octylphosphine oxide	$LTiCl_2 \cdot C_{24}H_{51}PO$	7.22(7.07)	15.49(15.65)



I

evidence for strong chelation of the CO group to titanium is seen from the shift in the carbonyl absorption at 1660 in the free ligand to 1610 in the compounds.

In the IR spectra of addition compounds with nitrogen bases, the bands for coordinated C=N groups of aromatic tertiary bases should appear around 1600 cm^{-1} ; but these vibrations could not be identified from those of LTiCl_3 due to the complexity of the spectra in this region. However, in the pyridine N-oxide adducts, the ν N-O at 1265 in the ligand was shifted to 1220 cm^{-1} (ref. 6). In the tri-*n*-octyl-phosphine oxide adducts ν P=O in the ligand at $1350\text{--}1260\text{ cm}^{-1}$ was shifted to 1220 cm^{-1} in the adducts due to coordination through phosphoryl oxygen. All these changes in the behaviour of ν N-O and ν P=O point out⁷ the coordination of the ligands to the metal atom. A hexa-coordinated structure (I) may be assigned to these addition compounds.

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Synthesis of Pure Salts of Pentaamminemonothiocyanatoruthenium(III) & Tetraamminedithiocyanatoruthenium(III)

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A synthetic procedure for obtaining the salts of $[\text{Ru}(\text{NH}_3)_5\text{SCN}]\text{X}_2$ and $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]\text{X}$ ($\text{X} = \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4$) in high purity is described for the first time.

IN the reactions of ammonium thiocyanate with pentaamminemonohaloruthenium(III) halides between 65°C and 80°C , it was shown¹⁻³ that two catio-

nic species, viz. $[\text{Ru}(\text{NH}_3)_5\text{SCN}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]^+$ and an anionic species of Ru(III) were simultaneously formed in solution. The cationic species were however, difficult to isolate in the pure form. In this note a synthetic procedure for obtaining pure cationic species is described for the first time.

Ammonium thiocyanate (2g) was dissolved in an aqueous solution (15 ml) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (0.2 g). The solution was stirred for 3 hr at $65\text{--}75^\circ$ whereby the colour of the solution changed to deep reddish violet. After cooling it to room temperature, a red violet compound containing the cationic species, $[\text{Ru}(\text{NH}_3)_5\text{SCN}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]^+$ along with anionic species of Ru(III) precipitated out by adding conc. HCl (~ 5 ml). It was centrifuged, washed with a little cold water, excess of ethanol and ether and dried *in vacuo*. The double salt thus obtained was dissolved in minimum amount of water and the solution passed through an anion exchange resin (Dowex 1-X8) column ($25\text{ cm} \times 1\text{ cm}$) in the chloride form at a rate of 0.5 ml/min and the column washed with water until the eluent was colourless (~ 50 ml). The eluent was concentrated to about 10 ml either at room temperature or in a lyophilizer and 2-3 ml conc. HClO_4 added to the resulting solution to precipitate the perchlorate salts of the cation species. It was centrifuged, washed with ethanol, ether and dried *in vacuo*. The dried compound (~ 100 mg) was dissolved in minimum quantity of water (~ 20 ml) and passed through a column ($100\text{ cm} \times 1\text{ cm}$) of Sephadex G-10. The column was eluted with a 0.001% aq. solution of HClO_4 with an elution rate of $3\text{--}4\text{ ml/hr}$. whereupon two bands appeared on the column; at the higher elution rate, the bands did not separate. The two bands were separately collected and the compound from the first eluent precipitated in near quantitative yield by adding a conc. HClO_4 (1 ml). It was centrifuged, washed with a little cold water, ethanol, ether and dried *in vacuo*. It analysed for $[\text{Ru}(\text{NH}_3)_5\text{SCN}](\text{ClO}_4)_2$; yield 60 mg.

From the eluent of second band the cationic species $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]^+$ could not be precipitated out by adding conc. acid probably because of its very high solubility. It was, therefore, concentrated in a lyophilizer to near dryness and to the residue 1-2 ml of conc. HClO_4 was added, whereupon $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]\text{ClO}_4$ partially precipitated out by keeping the solution at 0°C for about 2 hr. The precipitate was centrifuged, washed with a little cold ethanol and finally with ether (The washing of the dithionic species should be carried out very carefully). The precipitate was dried *in vacuo* and analysed for $[\text{Ru}(\text{NH}_3)_4(\text{SCN})_2]\text{ClO}_4$; yield 30-40 mg.

The bromo-, iodo-, nitrate-salts of both these cations were precipitated by dissolving the perchlorate salts in a small quantity of water and precipitating the corresponding salt by adding conc. HBr, HI and NaNO_3 respectively. Or the salts could also be synthesized by the same procedure as noted above except that the cationic salts were passed through anion exchanger in the corresponding bromo-, iodo- or nitrate- form. The eluents were dried in a lyophilizer.