Reaction of Aliphatic Amines with Tin IV Tetrachloride - Part II Synthesis of Tetrachlorobis (methylamine) Tin IV

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Summary: A 1:2 adduct of tin tetrachloride with methylamine is reported. When pure monomethylamine gas reacts with tin (IV) tetrachloride in the molar ratio (CH_3NH_2 : $SnCl_4$) 4:1 and 6:1 in carbon tetrachloride, only one substance is obtained which is independent of the reaction time. The product is the simple 1:2 adduct of tin (IV) chloride and methylamine. The paper describes the synthesis and properties of this adduct including its i.r. spectrum.

Introduction

The reaction of monoethylamine has been studied by many authors [1,2,3]. The reaction of excess of monomethylamine with $SnCl_4$ as carried out by the author gave a variety of products depending on the reaction time [4]. The end product was produced after two hr. One molecule of the evolved hydrogen chloride combines with the excess of methylamine, thus resulting in methylamine hydrochloride molecule, which rearranges on the product. The initial step was the addition of two molecules of methylamine to the Sn-atom, the second is the aminolysis and this was the reason of the exothermic nature of the reaction and finally the rearrangement of the methylamine hydrochloride on the complex as illustrated in the mechanism of the reaction [4].

A mixture of compounds were produced, which was very difficult to separate.

From this experience, the author studied the reaction of tin (IV) chloride with methylamine in a stiochiometric amount.

$$SnCl_4 + 2CH_3NH_2 \longrightarrow SnCl_4.2NH_2CH_3 \quad (1)$$

$$SnCl_4.2NH_2CH_3 + CH_3NH_2 \longrightarrow (CH_3NH)SnCl_3.2NH_2CH_3 + HCl \quad (2)$$

$$NH_2CH_3 + HCl \longrightarrow NH_3CH_3Cl \quad (3)$$

$$SnCl_4 + 4CH_3NH_2 \longrightarrow (CH_3NH)SnCl_3.2NH_2CH_3 + CH_3NH_3Cl \quad (4)$$

Scheme 1

Experimental

Monomethylamine gas was purified and dried as described in Part I [4]. In a 500 ml two-necked round bottom flask assembled with Liebig's condenser and gas inlet tube either 5.57 g (0.022 M) or 3.86 g (0.015 M) water-free $SnCl_4$ are dissolved in about 250 ml CCl_4. A 2-litre flask was mounted over the Liebig's condenser which was air evacuated. Through a gasometer apparatus (Fig. 1) an amount (2L) of pure and dried monomethylamine gas was allowed to react slowly with the tin (IV) tetrachloride.

The exact amount of gas required were passed by means of the gasometer technique shown in Fig. 1. The reaction time was between 15 - 20 hr. The reaction was not exothermic and no evolution of gas was noticed. By repeating the reaction in both ratio 4:1 and 6:1 of CH_3NH_2 to $SnCl_4$ the same product was obtained.

Results and Discussion

Since the reaction was not exothermic, no aminolysis takes place. Two molecules of methylamine bonded to the tin atom of the tin(IV) tetrachloride

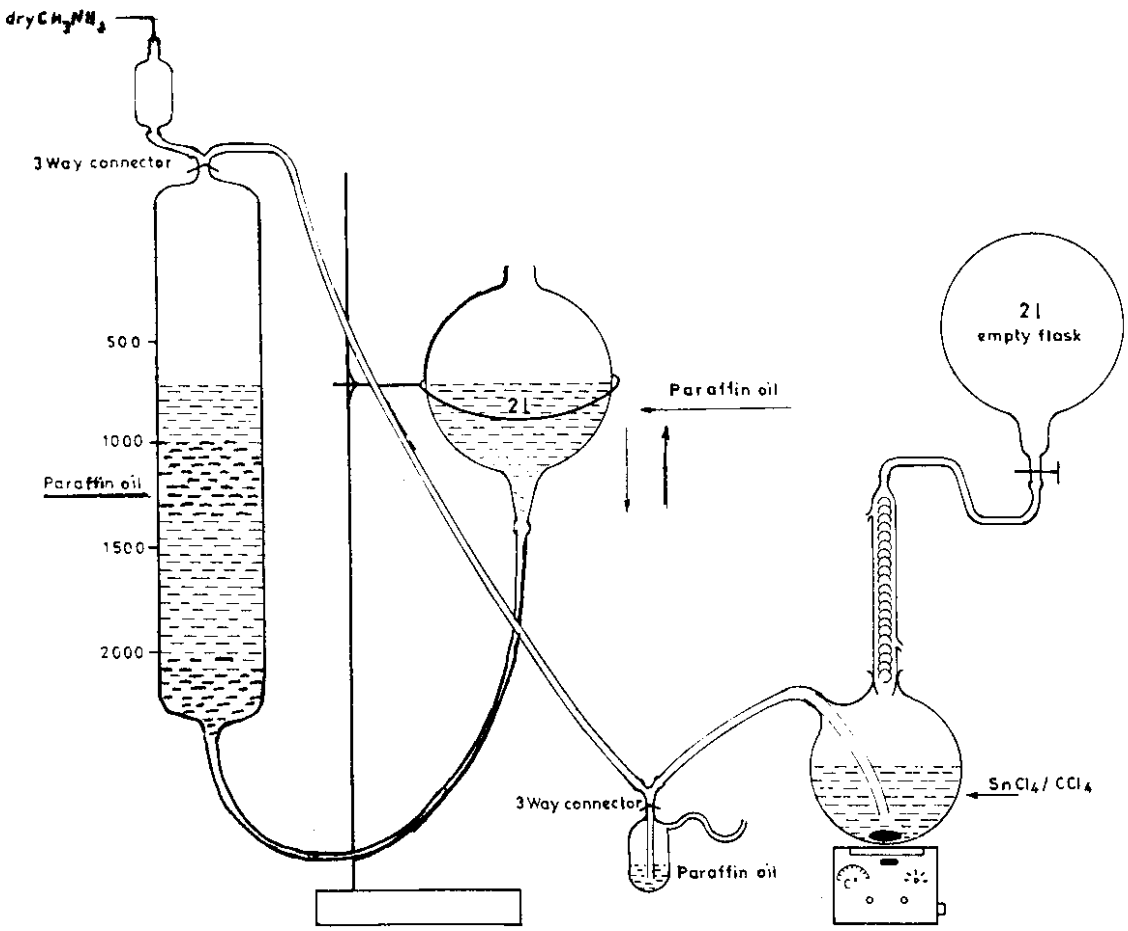
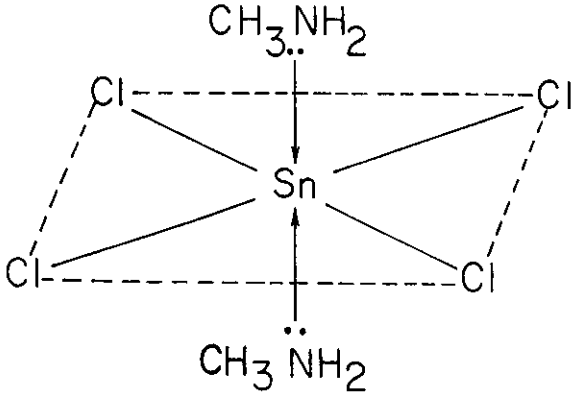


Fig.1 Gasometer

to form a 1:2 adduct. This complex raises the coordination number of tin from 4 to 6. The product is consistent on repeating the reaction and it is time-independent. The suggested structure is given as I.

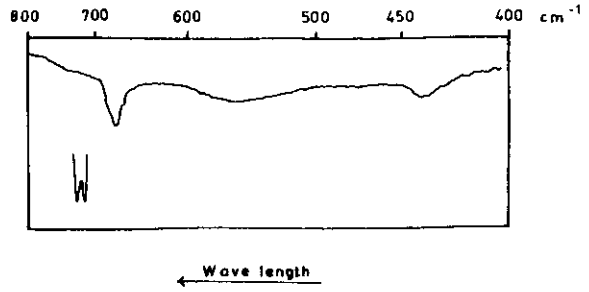


(I)

$SnCl_4 . 2CH_3NH_2$

The exact arrangement of ligands is still open [5], although the trans configuration of ligands of similar synthesized complexes [6] had been suggested on basis of its x-ray crystallography [7]. The adduct is fine powdery substance, but it is air moisture sensitive. At 140°C the adduct loses some CH_3NH_2 and it melts at 220°C with decomposition. It dissolves only in formic acid. The i.r. spectrum is given.

i.r. spectrum of $SnCl_4 . 2CH_3NH_2$(I) in KBr (4000 - 400 cm^{-1}).



The bands at 3200 and 3250 cm^{-1} are assigned to NH vibration, the broad band at 3000 cm^{-1} is attributed to asym. and sym. CH_3 vibration. The trough band between 500 and 600 cm^{-1} is assigned to N-Sn-N vibration [8]. Those bands at 1570 cm^{-1} and 1035 cm^{-1} are assigned as ν NH and ν(C-N) + νNCN respectively.

The elemental analysis of adduct gives the molecular formula $C_2H_{10}N_2Cl_4Sn$ Calc. 7.44% C;, 3.34% H; 8.67% N; 43.95% Cl and 36.7% Sn found 7.38% C;, 3.24% H; 8.18% N; 44.10% Cl and 36.3% Sn which supports the 1:2 adduct $SnCl_4 . 2CH_3NH_2$.

Acknowledgement

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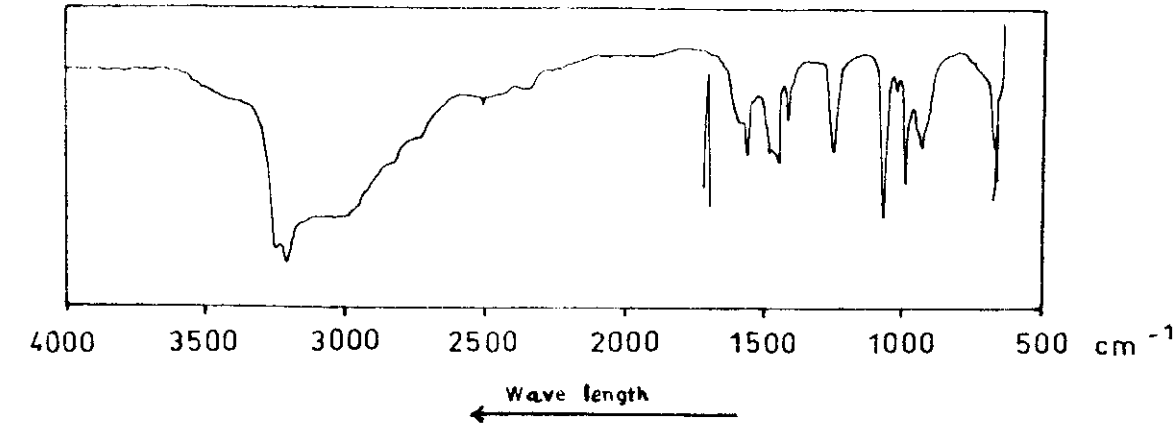

References

1. G.W.A.Fowles, Proceedings of Symposium on Chemistry of Coordination Compounds: Agra, India, Part 1, 41 (1960).
2. R.T. Cowdell and G.W.A. Fowles, *J.Chem.Soc., 2522 (1960).*
3. E. Bannister and G.W.A. Fowles, *J.Chem.Soc., 310 (1959).*
4. R.H. Abu-Samn, Proceedings of the Ist Symposium of Tin Anticancer Research, Scranton, PA, USA, May (1984).
5. R.H. Abu-Samn, *J.Chem.Soc.Pak., 5 23 (1983).*
6. R.H.Abu-Samn and H.P. Latscha, *Chemiker-Ztg, **96**, 222 (1972).*
7. B.Kruss, Ph.D. Dissertation, Heidelberg (1972).
8. W.P. Neumann, The Organic Chemistry of Tin, Interscience Publishers, John Wiley & Sons, Bristol, U.K(1970)