

SOME NEW CYCLOPENTADIENYLS AND INDENYLS OF ANTIMONY (III) CONTAINING AROMATIC HYDROCARBON BRIDGE.

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ABSTRACT

Some cyclopentadienyls and indenyls of antimony (III) involving aromatic hydrocarbon bridge between two antimony atoms have been synthesized and characterized on the basis of analytical and IR data. Some possible suggestions regarding the structures of these complexes on the basis of IR spectra have been given.

INTRODUCTION

VERY few cyclopentadienyls of Sb (III) have been mentioned in the literature. $(C_5H_5)_3Sb$; a yellow-coloured substance, was obtained for the first time by treating $SbCl_3$ with NaC_5H_5 in diethyl ether or pentane at low temperature¹. Other reported cyclopentadienyls include $Sb_2(C_5H_5)_4$, $(CH_3)_2Sb(C_5H_5)^3$, and $(C_5H_5)SbCl_2$ ⁴. Different methods and reactions have been tried in the preparation of these cyclopentadienyls. Antimony trichloride is itself not stable in air, and the reported cyclopentadienyls are also unstable. $SbCl_3$ forms a number of stable adducts with a variety of compounds, which can easily be handled in air. In this communication we have used some aromatic hydrocarbon adducts for the preparation of cyclopentadienyls and indenyls of Sb(III). The products obtained are comparatively stable. Work on reactions with other types of adducts is in progress.

Antimony trichloride forms a novel adduct with naphthalene, $2SbCl_3 \cdot (C_{10}H_8)$, which is quite stable and its structure is found to consist of the two $SbCl_3$ molecules joined by naphthalene molecule bridge⁵. Menshutkin has shown that a series of complexes of SbX_3 with aromatic hydrocarbons or substituted hydrocarbons could be made⁶. An extensive study of SbX_3 aromatic hydrocarbon complexes to determine the nature of bonding forces between the constituents was made⁷. A knowledge of the bonding is important in view of the known catalytic properties of $SbCl_3$ in Friedel-Crafts reaction and the possible relation of these structures to the reaction intermediates⁸. In this communication, preparation of 2:1 complexes of $SbCl_3$ with naphthalene, anthracene and phenanthrene, and their cyclopentadienyl and indenyl derivatives have been reported. It has been observed that the aromatic hydrocarbon bridge persists in the resulting complexes. Furthermore, cyclopentadienyl antimony dichloride has been found to form similar bridged complexes on treatment with the above mentioned hydrocarbons. The complexes are characterized and identified by elemental analysis and IR Spectra.

EXPERIMENTAL

Since all the reactions were carried in non-aqueous medium, they were carried out in dry atmosphere using dry solvents. $SbCl_3$ of A. R. grade was used for various synthesis. Other chemicals used were of extra-pure quality. Antimony was volumetrically estimated iodometrically⁹, Cl, C, and H were estimated semimicroanalytically.

(I) Preparation of antimony trichloride-aromatic hydrocarbon complexes

$SbCl_3$ (2.28 g) was dissolved in dry hot petroleum ether (80 ml). To this, dry powdered aromatic hydrocarbon (naphthalene, anthracene, phenanthrene) were slowly added in molar ratio 2:1. The reaction mixture was refluxed for about 2 hr. The resulting solution was reduced to about 20 ml and then kept for crystallization. The light-coloured crystals were recrystallized with hot petroleum ether. The complexes are quite stable and kept in dry atmosphere.

(II) Preparation of dicyclopentadienyl (or bisindenyl) μ -aromatic hydrocarbono diantimony (III) tetrachlorides from (I)

To a solution of 1 g of each of the above complexes in 40 ml of dry tetrahydrofuran, a solution of sodium cyclopentadienide (or sodium indenide) was slowly added in molar ratios of 1:2 with constant stirring for 6-7 hr; white precipitate of NaCl separated out. The reaction mixture was allowed to settle for 24 hr and then filtered. The dark orange to brown coloured mother liquors were evaporated under reduced pressure. The orange-to-reddish brown semisolids were well washed with petroleum ether (4-5 times) and then dried. The complexes are low melting solids, insoluble in water and cold benzene. The above complexes were also obtained when $C_5H_5SbCl_2$ or $C_9H_7SbCl_2$ and the aromatic hydrocarbon were stirred in tetrahydrofuran for 6-7 hr at 40-45° C. The reaction mixture was kept for 24 hr and then filtered. The coloured mother

TABLE 1

Analytical data of the aromatic hydrocarbon bridged complexes and their cyclopentadienyls and indenyls derivatives.

Compound	Mol. wt. (calc) found	% (calc) found			
		Sb	C	H	Cl
2SbCl ₃ .C ₁₀ H ₈ (Naphthalene)	(584.4) 593.27	(41.66) 41.34	(20.52) 20.21	(1.36) 1.40	(36.44) 36.53
2SbCl ₃ .C ₁₄ H ₁₀ (Anthracene)	(634.4) 641.52	(38.38) 38.57	(26.48) 26.29	(1.57) 1.61	(33.57) 33.68
2SbCl ₃ .C ₁₄ H ₁₀ (Phenanthrene)	(634.4) 646.31	(38.38) (38.23)	(26.48) (26.40)	(1.57) (1.43)	(33.57) 33.42)
(C ₅ H ₅) ₂ Sb ₂ Cl ₄ .C ₁₀ H ₈ (Naphthalene)	(643.5)	(37.83)	(37.29)	(3.10)	(22.37)
(from adduct)	651.62	37.67	37.41	3.20	22.13
(from C ₅ H ₅ .SbCl ₂)	653.78	38.02	37.39	3.17	22.58
(C ₉ H ₇) ₂ Sb ₂ Cl ₄ .C ₁₀ H ₈ (Naphthalene)	(743.5)	(32.75)	(45.19)	(2.95)	(19.09)
(from adduct)	760.31	32.33	45.34	2.84	19.39
(from C ₉ H ₇ .SbCl ₂)	756.42	32.61	44.98	2.99	18.97
(C ₅ H ₅) ₂ Sb ₂ Cl ₄ .C ₁₄ H ₁₀ (Anthracene)	(693.5)	(35.11)	(41.52)	(2.88)	(20.47)
(from adduct)	702.34	35.33	41.31	2.71	20.23
(from C ₅ H ₅ .SbCl ₂)	698.93	35.41	41.63	2.73	20.31
(C ₉ H ₇) ₂ Sb ₂ Cl ₄ .C ₁₄ H ₁₀ (Anthracene)	(793.5)	(30.68)	(48.39)	(3.02)	(17.89)
(from adduct)	787.49	30.43	48.52	3.10	17.51
(from C ₉ H ₇ SbCl ₂)	798.37	30.71	48.56	2.98	17.71
(C ₅ H ₅) ₂ Sb ₂ Cl ₄ .C ₁₄ H ₁₀ (Phenanthrene)	(693.5)	(35.11)	(41.52)	(2.88)	(20.47)
(from adduct)	698.75	35.27	41.73	2.79	20.32
(from C ₅ H ₅ SbCl ₂)	701.23	34.91	41.71	2.81	20.51
(C ₉ H ₇) ₂ Sb ₂ Cl ₄ .C ₁₄ H ₁₀ (Phenanthrene)	(793.5)	(30.68)	(48.39)	(3.02)	(17.89)
(from adduct)	797.14	30.52	48.63	3.13	17.54
(from C ₉ H ₇ SbCl ₂)	799.23	30.71	48.71	3.14	17.97
(C ₅ H ₇) ₄ Sb ₂ Cl ₂ .C ₁₀ H ₈ (Naphthalene)	(702.5) 711.73	(34.66) 34.51	(51.24) 51.03	(3.98) 3.82	(10.10) 10.23
(C ₉ H ₇) ₄ Sb ₂ Cl ₂ .C ₁₀ H ₈ (Naphthalene)	(902.5) 915.32	(26.98) 26.81	(61.16) 61.32	(3.98) 4.03	(7.86) 7.73
(C ₅ H ₅) ₄ Sb ₂ Cl ₂ .C ₁₄ H ₁₀ (Anthracene)	(752.5) 761.32	(32.35) 32.13	(54.21) 54.55	(3.98) 4.02	(9.43) 9.33
(C ₉ H ₇) ₄ Sb ₂ Cl ₂ .C ₁₄ H ₁₀ (Anthracene)	(952.5) 963.21	(25.56) 25.41	(62.99) 62.73	(3.98) 3.81	(7.45) 7.56
(C ₅ H ₅) ₄ Sb ₂ Cl ₂ .C ₁₄ H ₁₀ (Phenanthrene)	(752.5) 763.25	(32.35) 32.17	(54.21) 54.61	(3.98) 3.79	(9.43) 9.59
(C ₉ H ₇) ₄ Sb ₂ Cl ₂ .C ₁₄ H ₁₀ (Phenanthrene)	(952.5) 967.34	(25.56) 25.39	(62.99) 63.17	(3.98) 3.83	(7.45) 7.58

liquor was evaporated to dryness under reduced pressure and the residue on treatment with petroleum ether gave products identical with complexes II.

(III) *Preparation of tetracyclopentadienyl (or tetraindenyl)- μ -aromatic hydrocarbono diantimony (III) dichlorides.*

The reactions of complex I with sodium cyclopentadienide (or sodium indenide) in molar ratio 1:4 in tetrahydrofuran was carried out, by refluxing them for 4-6 hr. The reaction mixture was cooled, filtered and the coloured mother liquors were evaporated to dryness under reduced pressure. The residues were washed with dry petroleum ether when brownish coloured compounds were obtained. They were insoluble in benzene and decomposed on heating.

Analytical data of the complexes are summarized in table I. The cyclopentadienyl and the indenyl complexes are generally liquids or semisolids under ordinary conditions. They are readily attacked by acids, alkalis and water. They are also thermally not very stable.

DISCUSSION

Antimony trichloride is believed to possess a distorted tetrahedral distribution of electron pairs around antimony atom. The molecule has pyramidal geometry with one vertex occupied by a lone pair¹⁰. Its complex with naphthalene in 2:1 ratio contains antimony atoms π -bonded to naphthalene ring. The structure can be described as a pseudo π -allene complex⁵. Anthracene and phenanthrene complexes with SbCl_3 could be assigned identical structures as the changes in Sb-Cl bond frequency and C-C bond frequencies could be explained by the change in hybridization or coordination of antimony and the change in π -bond order in the anthracene/phenanthrene respectively. The spectra of the complexes differ from that of the components by a significant redistribution of the intensities and a shift in the frequencies. New bands were observed in some parts of the spectrum, and some previously single bands were found split. The C-H stretch appears in the two distinct regions ~ 3020 – 3050 and 2950 – 2960 cm^{-1} ; and besides there are a few more weak or medium peaks or shoulders observed in this range. The C-H stretch split points out the difference in the various H atoms in the molecules on the naphthalene, anthracene or phenanthrene rings. The decrease in C-C skeletal vibrations and appearance of new lines in the region ~ 1610 , ~ 1440 and ~ 1380 cm^{-1} may be attributed to the fact that these complexes are formed by means of the π -electrons¹¹. The C-H out of plane bending mode appears in the region ~ 750 – 880 cm^{-1} (up to 6 bands)

for naphthalene complexes, two strong bands at ~ 880 and 720 cm^{-1} with other bands for anthracene complex, and in the range 900 – 650 cm^{-1} (four bands with multiples) for phenanthrene complex. The C-H in plane bending frequency occurs in the form of many bands between 960 – 1235 cm^{-1} for naphthalene complex, in two groups ~ 1140 and 1055 cm^{-1} for anthracene complex, and many bands in the range 1500 – 900 cm^{-1} for phenanthrene complex¹². Thus it appears that the aromatic hydrocarbon molecule is considerably distorted. The longest Sb-Cl bond in the SbCl_3 molecule points directly at the concentration of higher electron density on the aromatic hydrocarbon molecule. The donation of electrons from the π -system to the antimony, results in an sp^3d hybridization of the the antimony electrons. The equatorial plane is made of the remaining two chlorines and the lone pair. The electron donated from the π -system fills the axial position. The lone pair points over the centre of the aromatic ring and is ideally situated for back bonding to the π -system. The IR spectra point out that the interaction between antimony and hydrocarbon is not very strong, though it is strong enough to produce considerable π -electron localization. The bond, therefore, may be thought of, as only partial filling of the axial sp^3d antimony orbital from aromatic hydrocarbon π -system. The hydrocarbon molecule behaves as a π -allene like complexing agent producing pseudo π -allene complexes. This is also confirmed by Sb-Cl stretch frequencies appearing at ~ 345 , 325 , 295 , 235 cm^{-1} , which are assigned to trigonal bipyramidal distribution of electron pairs around antimony in $[\text{SbCl}_4]$ complex with a lone pair of electrons at the equatorial position¹³. The new lines observed in the regions of Sb-Cl stretching mode may be attributed to the formation of bonds between SbCl_3 molecule and the aromatic hydrocarbon molecule.

The proposed structure of the complexes I, indicates the weakening of the axial Sb-Cl bond, making it easily attackable. Hence when these complexes were treated with sodium cyclopentadienide or sodium indenide, the axial chlorine was readily substituted by cyclopentadienyl or indenyl ring giving complexes II. IR spectra of complexes II showed all the bands of complexes I; in addition to the bands present at ~ 3070 cm^{-1} (C-H stretching); ~ 1085 and 1450 cm^{-1} (C-C stretching); ~ 995 cm^{-1} (C-H in plane bending); ~ 825 and 775 cm^{-1} (C-H out of plane bending); 435 cm^{-1} (ring tilt); and 355 cm^{-1} (M-ring stretching) could be assigned to a π -bonded cyclopentadienyl group¹⁴ and additional bands at ~ 1360 cm^{-1} (phenyl C-H stretch), ~ 1610 cm^{-1} (C-C stretch), ~ 740 cm^{-1} (C-H out of plane bending) and ~ 705 cm^{-1} (methylene rocking) for π -bonded indenyl group¹⁵. Since the

equatorially situated lone pair on antimony is over the π -electron cloud of the cyclopentadienyl and indenyl ring, it can provide back bonding to the ring—a situation for π -bonded cyclopentadienyl or indenyl ring. Hence the cyclopentadienyl or indenyl rings are delocalized π -bonded to antimony, further confirmed by the absence of the band at $\sim 2900\text{ cm}^{-1}$ and the presence of a single band $\sim 1085\text{ cm}^{-1}$ pointing out the presence of parallel cyclopentadienyl or indenyl rings¹⁶.

IR spectra of complexes III were almost identical with those of complexes II with a few differences. Band $\sim 2950\text{ cm}^{-1}$ points out the presence of σ -bonded cyclopentadienyl or indenyl ring also. Perhaps a rapid interconversion of π - and σ -bonded rings occurs in these complexes as has been pointed out for $\text{Sb}(\text{C}_5\text{H}_5)_3^{1,3}$. Only one Sb-Cl band appears $\sim 280\text{ cm}^{-1}$ the two cyclopentadienyl or indenyl rings attached to one antimony atom probably become canted in these complexes as is shown by the appearance of a characteristic doublet of medium intensity at $\sim 1050\text{ cm}^{-1}$ and two medium intensity bands $\sim 850\text{--}890\text{ cm}^{-1}$ which are associated with the ring deformation in compounds having this geometry¹⁷.

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ANNOUNCEMENT

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Prof. C. N. R. Rao, Chairman, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, has been elected President-elect of the International Union of Pure and Applied Chemistry, during the general assembly held at Copenhagen, Denmark, recently. Prof. Rao, will take over as the President in 1985 and will be Vice President till then.

He is the first Indian scientist to be elected to such a high office.

Prof. Rao, is the President of the Current Science Association, a member of the Science Advisory Committee to the Union Cabinet and Vice President of the Indian Academy of Sciences and the Indian National Science Academy.