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Synthesis and Characterization of Some Dicarboxylato and Salicylato Derivatives of Antimony Trichloride Adducts

P. DABAS † and M.K. RASTOGI*
Department of Chemistry
Hindu College, Delhi-110 007, India

Dicarboxylato and salicylato chelates of some antimony trichloride adducts have been prepared. The antimony trichloride adducts used were with anthracene, aniline, benzamide, pyridine, thiourea and DMSO. The disodium salts of oxalic, succinic, adipic, tartaric, salicylic and phthalic acids were used. The physical characteristics and IR, UV spectra of the complexes are reported. The nature of the metal-carboxyl group linkage is discussed.

INTRODUCTION

Some stable antimony trichloride adducts with Lewis bases on treatment with sodium salts of dicarboxylic acids and salicylic acid in 1 : 1 molar ratio gave the corresponding dicarboxylato and salicylato derivatives in which two chlorine atoms of the antimony trichloride part are substituted by the dicarboxylate or the salicylate residue. In case of anthracene adduct one antimony trichloride molecule is knocked off. The ν_{sym}(O—C—O) and ν_{asym}(O—C—O) values are helpful in establishing the nature of the metal-carboxylato group bonding.

EXPERIMENTAL

Preparation of oxalato derivative of antimony trichloride-anthracene adduct ($C_{14}H_{10} \cdot 2SbCl_3$)

1.50 G antimony trichloride-anthracene adduct was dissolved in 40 mL hot chloroform; 0.35 g sodium oxalate was added to it with shaking. The reaction mixture was refluxed for 10 h. A light green residue was obtained and separated from the mother liquor by filtration. It was washed with petroleum ether and recrystallized from hot THF-ether mixture. The analysis (Table-1) corresponded to the formula $(COO)_2SbCl \cdot C_{14}H_{10}$.

The derivatives of antimony trichoride-benzamide adduct were similarly prepared.

Preparation of phthalato derivative of antimony trichloride-pyridine adduct ($SbCl_3 \cdot 2C_5H_5N$)

1.40 G antimony trichloride-pyridine adduct, 0.76 g sodium phthalate and 20

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†Department of Chemistry, Gargi College, New Delhi-110 049, India.

mL DMF were taken in a flask. The reaction mixture was kept at 50°C for 10 h cooled and kept overnight. The white residue was separated from the mother liquor by filtration. The product was well washed with petroleum ether and recrystallized from hot THF-ether mixture. The analytical results (Table-1) of the compound corresponded to the composition $C_6H_4(COO)_2SbCl\cdot 2C_5H_5N$.

The dicarboxylato derivatives of antimony trichloride-aniline/thiourea/DMSO adducts were similarly obtained.

TABLE-1
ANALYTICAL DATA AND SOME PHYSICAL CHARACTERISTICS OF DICARBOXYLATO AND SALICYLATO DERIVATIVES OF SOME ANTIMONY TRICHLORIDE ADDUCTS

Compound (adduct used)	Mol. wt. Found (Calc.)	Colour (Dec. Temp.)	Found % (Calc.)		
			Sb	Cl	N
$(COO)_2SbCl\cdot C_{14}H_{10}$ (anthracene, oxalato)	420.8 (423.0)	Light green (171)	28.56 (28.72)	8.37 (8.49)	—
$C_6H_4(COO)_2SbCl\cdot C_{14}H_{10}$ (anthracene, phthalato)	495.6 (499.0)	Light green (174)	24.27 (24.35)	7.10 (7.03)	—
$(CH_2COO)_2SbCl\cdot 2C_6H_5NH_2$ (aniline, succinato)	452.2 (459.0)	White (151)	26.34 (26.47)	7.76 (7.73)	6.14 (6.10)
$(OC_6H_4COO)SbCl\cdot 2C_6H_5NH_2$ (aniline, salicylato)	473.2 (479.0)	White (148)	25.52 (25.36)	7.34 (7.41)	5.78 (5.84)
$(CH_2CH_2COO)_2SbCl\cdot 2C_6H_5CONH_2$ (benzamide, adipato)	538.3 (543.0)	White (129)	22.50 (22.38)	6.49 (6.54)	5.13 (5.16)
$(CHOHCOO)_2SbCl\cdot 2C_6H_5CONH_2$ (benzamide, tartarato)	542.3 (547.0)	White (136)	22.34 (22.21)	6.38 (6.49)	5.21 (5.12)
$(CHOH\cdot COO)_2SbCl\cdot 2NH_2CSNH_2$ (thiourea, tartarato)	452.3 (457.0)	Light brown (132)	26.35 (26.59)	7.83 (7.77)	12.06 (12.25)
$(OC_6H_4COO)SbCl\cdot 2NH_2CSNH_2$ (thiourea, salicylato)	438.93 (445.0)	Light brown (131)	27.21 (27.30)	8.12 (7.98)	12.46 (12.58)
$(CH_2CH_2COO)_2SbCl\cdot (CH_3)_2SO$ (DMSO, adipato)	375.6 (379.0)	White (118)	32.23 (32.06)	9.34 (9.37)	—
$(OC_6H_4COO)SbCl\cdot (CH_3)_2SO$ (DMSO, salicylato)	376.7 (371.0)	White (123)	32.58 (32.75)	9.39 (9.57)	—
$(CH_2CH_2COO)_2SbCl\cdot 2C_5H_5N$ (pyridine, adipato)	452.2 (459.0)	White (163)	26.28 (26.47)	7.58 (7.73)	5.97 (6.10)
$C_6H_4(COO)_2SbCl\cdot 2C_5H_5N$ (pyridine, phthalato)	473.7 (479.0)	White (180)	25.19 (25.36)	7.53 (7.41)	5.73 (5.84)

RESULTS AND DISCUSSION

The prepared compounds are white except those of anthracene and thiourea adducts. They decompose on heating (temp. range 115–180°C). They are hydrolysed by hot water, dilute mineral acids and alkalis. Their magnetic susceptibilities are low (0.02–0.03 BM) indicating that they are diamagnetic. Their molar conductivities are low (0.5–1.0 ohm^{-1} cm^{2} mol^{-1}) (Table-1) showing non-ionic character. The determined molecular weights point to the monomeric nature of the compounds.

In the IR spectra of anthracene complexes the ν(C—H) of the ring appeared at *ca.* 3040 and 2960 cm^{-1} besides few more weak and medium peaks in this region. The decrease in the C—C skeletal vibrations and appearance of new lines at *ca.* 1650, 1450 and 1375 cm^{-1} suggest that the hydrocarbon ring is attached to antimony through π-electrons.[1] The peaks due to δ(C—H) appeared at *ca.* 1150 and 1050 cm^{-1}, whereas π(C—H) may be assigned[2] at *ca.* 875 and 725 cm^{-1}. The ν(Sb—O) and γ(Sb—Cl) are assigned at *ca.* 510, 375, 340 and 280 cm^{-1} which overlap with ν(C—C) and chelate ring deformations.

The aniline bands in the IR spectra of the aniline complexes are assigned as a band at *ca.* 3450 cm^{-1} due to ν_{asym}(N—H), at *ca.* 3400 cm^{-1} due to ν_{sym}(N—H), at *ca.* 1610 cm^{-1} due to δ(N—H), at *ca.* 1050 cm^{-1} due to ξ_t(N—H) and at *ca.* 550 cm^{-1} due to ξ_W(N—H). The ν(C—N) appeared at *ca.* 1320 and 1200 cm^{-1}, somewhat lowered due to Sb—N bonding.[3] The ring ν(C—H) are assigned at *ca.* 3050, 3010, 1850 and 1725 cm^{-1}, the δ(C—H) at *ca.* 1150, 1100, 1020 cm^{-1}, and the π(C—H) at *ca.* 750 cm^{-1}. The ring skeletal vibrations[4] appeared at *ca.* 1600, 1580, 1480 cm^{-1}. A group of bands in the lower region at *ca.* 525, 410, 380, 340 and 280 cm^{-1} may be assigned to ν(Sb—O), ν(Sb—N), ν(Sb—Cl), ν(C—C) and chelate ring deformations overlapping with each other.

The benzamide complexes retain benzamide molecules is shown in their IR spectra with bands at *ca.* 3450 and 3300 cm^{-1} assigned to ν_{asym}(N—H) and ν_{sym}(N—H) respectively, at *ca.* 1630 cm^{-1} due to δ(N—H). The lowering of ν(C═O) to *ca.* 1530 cm^{-1} indicated that benzamide molecule is coordinated to antimony atom through oxygen atom.[5] The ν(C—N) appeared at *ca.* 1390 cm^{-1}. The aromatic rings ν(C—H) assigned at *ca.* 3000, 1600, 1580, 1520 and 1400 cm^{-1}, π(C—H) appeared at *ca.* 720 cm^{-1} and δ(C—H) are at *ca.* 1240, 1080, 1020 cm^{-1}. The two bands at *ca.* 500 and 460 cm^{-1} may be assigned to ν(Sb—O) probably one due to amide O—Sb and the other due to carboxylato O—Sb linkages. The bands at *ca.* 370, 350 and 275 cm^{-1} may be assigned to ν(Sb—Cl), ν(C—C) and chelate ring deformations overlping with each other.

The IR spectra of thiourea complexes showed peaks at *ca.* 3450, 3320 and 3250 cm^{-1} which may be assigned to ν_{asym}(N—H) and ν_{sym}(N—H) respectively. The composite bands due to δ(NH$_2$), ν(C—N) and ν(C═S) are assigned at 1630, 1460, 1390 and 1000 cm^{-1}. The band at *ca.* 700 cm^{-1} may be due to ν(C═S) with some contributions from δ(NCS). The lowering of ν(C═S) and rise in ν(C—N) supports the coordination of thiourea to antimony through sulphur atom.[6, 7] The ν(Sb—S) bands are assigned[8] at 380 and 170 cm^{-1} which overlap with the ν(Sb—O), ν(Sb—Cl), ν(C—C) and chelate ring deformations assigned at *ca.* 500, 360, 340 and 270 cm^{-1}.

The presence of DMSO molecule in its complexes is indicated by the bands in their IR spectra assigned as[9, 10] ν_{asym}(C—H) and ν_{sym}(C—H) of methyl group at *ca.* 2950 and 2875 cm^{-1}, δ(CH_3) at *ca.* 1350 and 1320 cm^{-1} and ξ_r(CH_3) at *ca.* 930 and 910 cm^{-1}. The ν(S=O) is assigned at *ca.* 980 cm^{-1} lowered due to coordination of DMSO to antimony through oxygen.[11] The ν(Sb=O) may be assigned at 490 and 450 cm^{-1} and ν(Sb—Cl) at *ca.* 350, 300, 250 cm^{-1} whch overlap with ν(C—C) and chelate ring deformations.

In the IR spectra of pyridine complexes the presence of pyridine is shown by the appearance of bands at *ca.* 3350 cm^{-1} due to ring ν(C—H) at *ca.* 1225, 1150, 1050 cm^{-1} due to δ(C—H) and at *ca.* 750, 710 cm^{-1} due to π(C—H).[12] The ν (ring) and the ring skeleton vibrations appeared at 1040 and 980 cm^{-1}. The δ (ring) and π (ring) bands are assigned at *ca.* 655 and 460 cm^{-1}. The shift of these vibrations to higher frequencies and almost no shift in high frequency vibrations indicate the attachment of pyridine through nitrogen atom.[13] The π (ring) overlapped with the ν(Sb—O), ν(Sb—N), ν(Sb—Cl), ν(C—C) and chelate ring deformations tentatively assigned at *ca.* 440, 375, 340 and 280 cm^{-1}.

In all the dicarboxylato and salicylato complexes the ν_{sym}(O—C—O) (1390–1275 cm^{-1}) and ν_{asym}(O—C—O) (1700–1675 cm^{-1}) are of interest since their position and separation helps in determination of the nature of bonding of the acidic group to antimony. The ν_{sym}(O—C—O) and ν_{asym}(O—C—O) for various complexes are assigned at *ca.* 1610 cm^{-1} and 1380 cm^{-1} for oxalato compound, *ca.* 1710 cm^{-1} and 1290 cm^{-1} for succinato compound, *ca.* 1690 cm^{-1} and 1280 cm^{-1} for adipato compounds, *ca.* 1380 cm^{-1} and 1700 cm^{-1} for tartrato complexes; *ca.* 1690 cm^{-1} and 1390 cm^{-1} for phthalato complexes, and *ca* 1700, 1400 or 1300 cm^{-1} for salicylato compounds. A comparison of these two frequencies with the ionic salts on one hand and covalent esters on the other hand shows that the carboxylate metal bond is covalent in nature. Absorption bands at *ca.* 1030 and 900 cm^{-1} indicate a metal to carboxylate link.[14]

The oxalato compounds showed a band at *ca.* 810 cm^{-1} which could be assigned to δ(O—C—O), the band at 890 cm^{-1} is due to ν(C—C) and the band at 1255 cm^{-1} may be due to ν(C—O) and ν(C=O). The alkane ν(C—H) in the succinato complexes appeared at *ca.* 3010 cm^{-1}, while δ(CH_2), ξ_w(CH_2) and ξ_r(CH_2) appeared at *ca.* 1400, 1320 and 920 cm^{-1} respectively. The alkane ν(C—H) in the adipato complexes appeared at *ca.* 2890 cm^{-1}, δ(CH_2) at *ca.* 1400 cm^{-1}, ρ_w(CH_2) at *ca.* 1310 cm^{-1}, and ξ_r(CH_2) at *ca.* 910 cm^{-1}. The alkene ν(C—H) in the tartrato complexes are assigned at 2880 cm^{-1}, δ(CH_2) at *ca.* 1400 cm^{-1}, ξ_w(CH_2) at *ca.* 1320 cm^{-1}, ξ_w(CH_2) at *ca.* 920 cm^{-1}.[15]

The shift in carbonyl frequencies of the tartarato complexes may be due to intramolecular hydrogen bonding between OH group and oxygen of the C=O group. This is supported by the appearance of a medium intensity band at *ca.* 1650 cm^{-1} and a broad but weak band at *ca.* 2675 cm^{-1} indicating that the second carbonyl group is involved in hydrogen bonding which is further supported by the lowering of ν(O—H) to *ca.* 3300 cm^{-1}.[16, 17] The frequency shift of

ν_{asym}(O—C—O) and ν_{sym}(O—C—O) from normal values in the phthalato complexes may be due to aryl conjugation.[17]

The peaks at *ca.* 260 and *ca.* 210 nm in the UV spectra of all the complexes may be due to charge transfer.

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