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Synthesis of Some Complexes of Antimony(III) with Polyhydric Phenols, Acid Amides and Indene

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Reactions of antimony trichloride with polyhydric phenols (catechol, resorcinol, quinol, pyrogallol and phloroglucinol) in presence of amides (formamide, dimethylformamide and urea) leads to the formation of complexes of the type $Sb(O_nPh)_2(A)_2Cl$. On treatment of these complexes with sodium indenide in THF yields indenyl derivatives of the type $Sb(O_nPh)_2(A)_2In$. These compounds on slow heating lose the amide molecule to give complexes of the type $Sb(O_nPh)_2In$. The complexes have been characterized by elemental analysis, IR and electronic spectra, molecular weight determination, conductivity measurements and magnetic susceptibility measurements. It is suggested that the indenyl ring is σ-bonded to the antimony in the first two types of complexes but there appears to be a transition between the σ-bonded and π-bonded character of the indenyl ring in the third type. The amide molecules enter into the coordination sphere of antimony and the polyhydric phenols behave as monoacid ligands. (Ph is the phenolic residue, n is 2 or 3, In is the indenyl group and THF is tetrahydrofuran.)

INTRODUCTION

A survey of the literature revealed that no work has been done on the complexes of antimony reported in this communication. Only a few cyclopentadienyl derivatives of antimony(III) are reported in the literature,[1–5] but no indenyl derivatives of antimony(III) are reported. Antimony trichloride is not stable in air but the prepared complexes can be easily handled in dry air. A knowledge of the bonding in these complexes is important from the point of view of the known catalytic properties of antimony trichloride in Fridel-Crafts reaction and other reactions. There may be a possibility of establishing some relation between the structures and bondings in these complexes and the mechanism of catalytic action of antimony trichloride in such reactions. Hence a systematic work on these complexes was carried out.

EXPERIMENTAL

Preparation of bis(dimethylformamide)dicatechoxyantimony(III) chloide

1.14 G (0.005 mol) antimony trichloride and 1.10 g (0.01 mol) catechol were stirred with 10 mL of dimethylformamide in 40 mL of benzene. The reaction mixture was gently refluxed for 6 h. After cooling it was filtered and the clear filtrate was concentrated by evaporation and then kept overnight in a desiccator.

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A greyish yellow solid was obtained which was separated by filtration under suction. It was washed with petroleum ether and dried. It was recrystallized from a dimethylformamide-THF mixture in 1:3 ratio. The analysis of the compound corresponded to the formula $Sb(O_2C_6H_5)_2[HCON(CH_3]_2Cl$.

Preparation of diformamidedicatechoxyantimony(III) chloride

1.23 G (0.003 mol) of bis(dimethylformamide) dicatechoxyantimony(III) chloride was well stirred into 15 mL of formamide and kept for 24 h at room temperature (24°C). The greyish solid was filtered by suction and washed 2–3 times with small amounts of fomamide and suction dried. The solid was recrystallized from a formamide-THF mixture in 1 : 3 ratio. It was washed with petroleum ether and dried. Its analysis corresponded to the formula $Sb(O_2C_6H_5)_2(HCONH_2)_2Cl$.

Preparation of diureadicatechoxyantimony(III) chloride

1.04 G (0.002 mol) of bis(dimethylformamide) dicatechoxyantimony(III) chloride and 0.25 g (0.004 mol) urea were shaken in 30 mL of dry alcohol and the reaction mixture was gently refluxed till all urea had dissolved (3–4 h). It was then filtred hot and after a little evaporation, was kept for crystallization. The grey solid was filtered off by suction, washed with benzene and dried. It was recrystallized from an alcohol-THF mixture (1 : 1). The solid on analysis was found to correspond to the formula $Sb(O_2C_6H_5)_2(NH_2CONH_2)_2Cl$.

The complexes with other phenols were prepared by a similar procedure. Some characteristics and analytical data of the complexes are given in Table-1.

Preparation of indenyl bis(dimethylformamide) dicatechoxyantimny(III)

1.04 G (0.002 mol) bis(dimethylformamide) dicatechoxyantimony(III) chloride was dissolved in 30 mL of THF and a solution of 0.27 g (0.002 mol) sodium indenide in THF was added to it with stirring. The mixture was refluxed for 1 h, cooled and filtered. The clear filtrate was evaporated to a small volume under reduced pressure and cooled. It was then treated with excess of petroleum ether when a red-brown solid separated out. It was filtered and recrystallized from an ether-THF mixture in 2 : 1 ratio. It was well washed with petroleum ether and dried. The analysis of the solid corresponded with the formula $Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2C_9H_7$.

The indenyl derivatives of the other diamidediphenoxyantimony(III) chloride were prepared by a similar procedure. Some characteristics and analytical data of these complexes are given in Table-2.

Preparation of indenyldicatechoxyantimony(III)

About 1.20 g (0.002 mol) of indenyl bis(dimethyl formamide) dicatechoxyantimony(III) was kept at *ca.* 60°C under reduced pressure for about 12 h. The residue was cooled and well washed with petroleum. ether. An orange-brown solid was obtained which was recrystallized from a petroleum ether-THF mixture in the ratio 5 : 1. The analysis of the solid corresponded to the formula $Sb(O_2C_6H_5)_2C_9H_7$.

TABLE-1
SOME CHARACTERISTICS AND ANALYTICAL DATA OF THE DIAMIDEDIPHENOXYANTIMONY(III) CHLORIDES

Compound (colour)	m.w. Found (Calcd.)	Decomp. temp. (°C)	Analysis %, Found (Calcd.)		
			Sb	Cl	N
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2Cl$ (catechol) (dull yellow)	522.7 (521.2)	91	23.23 (23.34)	6.93 (6.81)	5.22 (5.37)
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2Cl$ (resorcinol) (dirty white)	532.5 (521.2)	92	23.61 (23.34)	6.73 (6.81)	5.31 (5.37)
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2Cl$ (quinol) (pale yellow)	529.3 (521.2)	91	23.54 (23.34)	6.87 (6.81)	5.28 (5.37)
$Sb(O_3C_6H_5)_2[HCON(CH_3)_2]_2Cl$ (pyrogallol) (light brown)	562.7 (553.2)	93	21.83 (21.99)	6.37 (6.41)	5.14 (5.06)
$Sb(O_3C_6H_5)_2(HCON(CH_3)_2]_2Cl$ (phloroglucinol) (dull grey)	565.9 (553.2)	93	22.14 (21.99)	6.53 (6.41)	5.01 (5.06)
$Sb(O_2C_6H_5)_2[HCONH_2)_2Cl$ (catechol) (ash grey)	472.3 (465.2)	95	26.35 (26.16)	7.56 (7.63)	6.20 (6.01)
$Sb(O_2C_6H_5)_2(HCONH_2)_2Cl$ (resorcinol) (light brown)	477.5 (465.2)	94	26.43 (26.16)	7.73 (7.63)	6.18 (6.01)
$Sb(O_2C_6H_5)_2(HCONH_2)_2Cl$ (quinol) (pale yellow)	468.9 (465.2)	95	25.95 (26.16)	7.58 (7.63)	6.15 (6.01)
$Sb(O_3C_6H_5)_2(HCONH_2)_2Cl$ (pyrogallol) (dirty white)	503.4 (497.2)	93	24.53 (24.47)	7.02 (7.13)	5.71 (5.63)
$Sb(O_3C_6H_5)_2(HCONH_2)_2Cl$ (phloroglucinol) (ash grey)	507.6 (497.2)	92	24.62 (24.47)	7.25 (7.13)	5.78 (5.63)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2Cl$ (catechol) (grey)	503.4 (495.2)	93	24.32 (24.57)	7.23 (7.16)	11.19 (11.30)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2Cl$ (resorcinol) (light brown)	501.7 (495.2)	93	24.41 (24.57)	7.25 (7.16)	11.20 (11.30)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2Cl$ (quinol) (dirty pink)	506.8 (495.2)	95	24.68 (24.57)	7.19 (7.16)	11.48 (11.30)
$Sb(O_3C_6H_5)_2(NH_2CONH_2)_2Cl$ (pyrogalllol) (light brown)	530.3 (527.2)	94	22.88 (23.08)	6.81 (6.73)	10.72 (10.62)
$Sb(O_3C_6H_5)_2(NH_2CONH_2)_2Cl$ (phloroglucinol) (light brown)	533.7 (527.2)	92	22.91 (23.08)	6.87 (6.73)	10.76 (10.62)

TABLE-2
SOME CHARACTERISTICS AND ANALYTICAL DATA OF THE INDENYLDIAMIDEDIPHENOXYANTIMONY(III) COMPLEXES

Compound/colour	m.w. Found (Calcd.)	Decomp. temp. (°C)	Analysis %, Found (Calcd.)			
			Sb	C	H	N
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2(C_9H_7)$	607.3	64	20.13	53.59	5.19	4.73
(catechol) (brown)	(600.7)		(20.25)	(53.93)	(5.16)	(4.66)
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2(C_9H_7)$	612.9	61	20.29	53.76	5.21	4.71
(resorcinol) (red brown)	(600.7)		(20.25)	(53.93)	(5.16)	(4.66)
$Sb(O_2C_6H_5)_2[HCON(CH_3)_2]_2(C_9H_7)$	619.1	59	20.34	54.13	5.08	4.69
(quinol) (orange brown)	(600.7)		(20.25)	(53.93)	(5.16)	(4.66)
$Sb(O_3C_6H_5)_2[HCON(CH_3)_2]_2(C_9H_7)$	641.3	62	19.59	51.42	4.91	4.38
(pyrogallol) (brown)	(632.7)		(19.23)	(51.20)	(4.89)	(4.42)
$Sb(O_3C_6H_5)_2[HCON(CH_3)_2]_2(C_9H_7)$	644.2	63	19.09	51.11	4.73	4.39
(phloroglucinol) (dark red)	(632.7)		(19.23)	(51.20)	(4.89)	(4.42)
$Sb(O_2C_6H_5)_2(HCONH_2)_2(C_9H_7)$	552.3	66	22.28	50.87	4.13	5.09
(catechol) (red brown)	(544.7)		(22.34)	(50.67)	(4.22)	(5.14)
$Sb(O_2C_6H_5)_2(HCONH_2)_2(C_9H_7)$	556.7	60	22.23	50.48	4.29	5.07
(resorcinol) (brick red)	(544.7)		(22.34)	(50.67)	(4.22)	(5.14)
$Sb(O_2C_6H_5)_2(HCONH_2)_2(C_9H_7)$	560.4	58	22.27	50.73	4.31	5.11
(quinol) (grey brown)	(544.7)		(22.34)	(50.67)	(4.22)	(5.14)
$Sb(O_3C_6H_5)_2(HCONH_2)_2(C_9H_7)$	583.6	64	21.23	47.67	3.96	4.91
(pyrogallol) (brown)	(576.7)		(21.10)	(47.85)	(3.98)	(4.85)
$Sb(O_3C_6H_5)_2(HCONH_2)_2(C_9H_7)$	587.2	60	21.37	47.75	3.93	4.79
(phloroglucinol) (red brown)	(576.7)		(21.10)	(47.85)	(3.98)	(4.85)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2(C_9H_7)$	583.4	63	21.03	48.14	4.27	9.68
(catechol) (grey brown)	(574.7)		(21.17)	(48.02)	(4.35)	(9.74)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2(C_9H_7)$	588.3	59	21.23	48.25	4.29	9.63
(resorcinol) (brown)	(574.7)		(21.17)	(48.02)	(4.35)	(9.74)
$Sb(O_2C_6H_5)_2(NH_2CONH_2)_2(C_9H_7)$	580.1	56	21.09	48.22	4.41	9.82
(quinol) (red brown)	(574.7)		(21.17)	(48.02)	(4.35)	(9.74)
$Sb(O_3C_6N_5)_2(NH_2CONH_2)_2(C_9H_7)$	612.3	58	20.17	45.33	4.17	9.33
(pyrogallol) (dark brown)	(606.7)		(20.05)	(45.49)	(4.12)	(9.23)
$Sb(O_3C_6H_5)_2(NH_2CONH_2)_2(C_9H_7)$	619.4	60	20.21	45.58	4.16	9.36
(phloroglucinol) (red brown)	(606.7)		(20.05)	(45.49)	(4.12)	(9.23)

Other indenyldiphenoxydiamideantimony(III) complexes decompose as above to give the corresponding indenyldiphenoxyantimony(III) compounds. Some characteristics and analytical data of these complexes are given in Table-3.

TABLE-3
ANALYTICAL DATA OF THE INDENYLDIPHENOXYANTIMONY(III) COMPLEXES

Compound	Colour		m.w. Found (Calcd.)	Analysis %, Found (Calcd.)		
				Sb	C	H
$Sb(O_2C_6H_5)_2(C_9H_7)$ (catechol)	red brown	1	461.2	26.57	55.31	3.80
		2	468.6	26.63	55.27	3.78
		3	463.4	26.82	55.19	3.69
			(454.7)	(26.76)	(55.42)	(3.73)
$Sb(O_2C_6H_5)_2(C_9H_7)$ (resorcinol)	orange brown	1	465.3	26.85	55.53	3.68
		2	459.2	26.87	55.64	3.65
		3	469.9	26.64	55.59	3.81
			(454.7)	(26.76)	(55.42)	(3.73)
$Sb(O_2C_6H_5)_2(C_9H_7)$ (quinol)	brick red	1	464.3	26.66	55.33	3.80
		2	467.6	26.59	55.57	3.75
		3	471.2	26.55	55.28	3.79
			(454.7)	(26.76)	(55.42)	(3.73)
$Sb(O_3C_6H_5)_2(C_9H_7)$ (pyrogallol)	dark brown	1	493.2	24.83	51.41	3.45
		2	494.3	24.94	51.39	3.47
		3	498.7	25.27	51.58	3.52
			(486.7)	(25.00)	(51.77)	(3.49)
$Sb(O_3C_6H_5)_2(C_9H_7)$ (phloroglucinol)	red brown	1	497.3	25.14	51.48	3.46
		2	502.6	24.88	51.92	3.51
		3	503.8	25.22	51.67	3.48
			(486.7)	(25.00)	(51.77)	(3.49)

Note: 1, 2, and 3 are values found for complexes obtained from dimethylformamide, formamide and urea complexes respectively.

RESULTS AND DISCUSSIONS

Molecular weights of all the complexes suggest that they are monomeric. Electrical conductance studies (*ca.* 0.06 ohm^{-1} cm^{-2} mol^{-1} in dimethylformamide) show that they are essentially non-electrolytes. The magnetic susceptibilities of the complexes (*ca.* 0.02 BM) indicate that they are diamagnetic. The electronic spectra of the complexes show a single band in the region 25000–24000 cm^{-1} (E_{max} *ca.* 11000). The band could be assigned to charge transfer bands.[6]

All the complexes showed sharp bands at *ca.* 3450 cm^{-1} and 1150 cm^{-1} which may be assigned to free hydroxyl group due to O—H stretching and bending respectively.[7] The N—H stretching frequency of the amide group in the formamide and urea complexes appearing at *ca.* 3440 cm^{-1} overlaps with the O—H stretching frequency, but the presence of broad bands at *ca.* 3340 and 3200 cm^{-1} may be assigned to the N—H stretching mode. These bands are not present in the IR spectra of the dimethylformamide complexes. The band at *ca.* 1640 cm^{-1} is possibly the NH_2 deformation mode not observed in case of dimethyl formamide complexes. There are also bands in the range *ca* 1400–1360 cm^{-1}, the origin of which is not clear.[8] The lowering of the C=O stretching frequency to *ca.* 1500 cm^{-1} as compared to the free ligands (1685 cm^{-1} for urea, 1725 cm^{-1} for formamide and 1650 cm^{-1} for dimethylformamide) indicates that the amide ligands are coordinated to antimony through oxygen atom.[9] There occurs no appreciable change in the N—H stretching frequency which should have been lowered to *ca.* 3100 cm^{-1} if coordination of the amides would have occurred through nitrogen atom.

Further, coordination through oxygen atom reduces the chance of involvement of different tautomeric forms for the amides. This is supported by the IR spectra of the formamide and dimethylformamide complexes which show no change in the C—N stretching frequency and no bands at *ca.* 2700 cm^{-1} due to the aldehyde C—H stretching.[10] Actually a group of stretching frequencies are observed within the range 1400–1100 cm^{-1} which may be regarded as composite of the O—H deformations,[11] C—C skeletal mode, C—H in-plane deformation,[12] metal phenoxide stretching and C—N strechings.[13]. Only one Sb—Cl stretching mode appears at *ca.* 310 cm^{-1}.[14]

The 1, 2; 1, 3; 1, 4; 1, 2, 3 and 1, 2, 5 substituted phenyl rings are differentiated from their C—H stretchings, C—H out-of-plane deformation and absorption bands in the range 2000–1650 cm^{-1}. The IR spectra of the indenyl derivatives of the diamidediphenoxyantimony(III) chlorides are comparable to the spectra of indene with respect to the absorption of the indenyl group. The various stretching frequencies are assigned as: a broad weak band at *ca.* 3070 cm^{-1} due to symmetical C—H stretching, *ca.* 630 cm^{-1} due to C—H stretching, two or three weak bands in the range 1630–1600 cm^{-1} due to C=C (ring) stretching; medium bands at 1460, 1440, 1390 cm^{-1}, weak bands at *ca.* 1250 cm^{-1} and weak to strong bands at *ca.* 940 cm^{-1} due to C—H (ring) deformations or asymmetric ring breathing; weak bands at *ca.* 1200 cm^{-1} and a medium bands at 890 cm^{-1} due to ring deformations; weak to medium bands at *ca.* 1075 and 1020 cm^{-1} due to the perpendicular hydrogen wagging mode; two bands at *ca.* 750 and 720 cm^{-1} due to the parallel hydrogen wagging mode; a band at *ca.* 490 cm^{-1} due to the ring tilt; and bands in the range 400–250 cm^{-1} due to the metal-ring stretching.[15] A band at *ca.* 690 cm^{-1} may be due to the methylene rocking vibrations.[16] The band positions in the IR spectra of the complexes show similarities with those of the indene itself. Hence it appears that the indenyl group is σ-bonded to the antimony atom. The presence of weak to medium bands in the range *ca.* 2980–2950 cm^{-1} due to C—H asymmetric stretching, a weak to medium band at *ca.* 1626 cm^{-1} due to C=C stretching and a strong band at *ca.* 755 cm^{-1} due to C—H deformation support this suggestion.[1, 3, 15]

The IR spectra of the indenyldiphenoxyantimony(III) complexes are slightly different from the indenyldiamidediphenoxyantimony(III) complexes. That an amide group is not present in these complexes is indicated by the absence of bands at *ca.* 3450, 3340 and 3200 cm^{-1} due to N—H stretching, a band at *ca.* 1640 due to NH_2 deformation, and a band at *ca.* 1500 cm^{-1} due to oxygen bonded amide group (C=O stretching). The free O—H group stretching frequency appears at *ca.* 3450 cm^{-1} and the O—H deformation mode appears as a weak band at *ca.* 1160 cm^{-1}. The metal-phenoxy stretching appears at *ca.* 1410 cm^{-1}. The C—H symmetrical stretching appears as a broad band at *ca.* 3040 cm^{-1}, while the asymmetical C—H stretching bands appear as weak bands in the range 2950–2870 cm^{-1}. Hence it appears that the indenyl group is σ as well as π-bonded to the antimony atom or there occurs a transition between the two types. This may be understood if the structure of the complexes is assumed to have a distorted pyramidal geometry with sp^3 hybridized antimony atom. Both the phenyl rings of the two phenoxy groups and the ring of the indenyl group try to accept back the lone pair on antimony introducing a π-bond character in the metal-ring bonding. Further, there appears to be a transition of π-electrons from the indenyl ring to the phenoxy ring or vice versa through the vacant *d*-orbitals of the antimony atom providing stability and strength to the bonds. This suggestion is supported by the electronic spectra of the complexes which show two bands in the range 28400–28000 cm^{-1} (E_{max} *ca.* 9500) probably due to intraligand electronic transition.[17] More intensity of the colour of the complexes may be due to conjugation over the entire molecule and due to charge transfer. The observed low value of the magnetic susceptibility of these complexes (μ_{eff} 0.21 BM) may be explained on the basis of acquisition of partial paramagnetism by the antimony atom due to the electron transition through its vacant d-orbitals.[18]

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