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Reactions of Antimony(III) Chloride Adducts with Potassium Thiocyanate

R. SAXENA, S. GUPTA and M.K. RASTOGI*
Department of Chemistry
Hindu College, Delhi-110 007, India

A number of adducts of antimony trichloride have been prepared with O, N, S-donor atoms. These adducts have been treated with KCNS in THF when substitution of the chlorine atoms in the adduct occurs with SCN group resulting in the formation of antimony trithiocyanate adducts. The ambidentate SCN group attaches to antimony through nitrogen in some complexes (naphthalene, anthracene, phenanthrene, pyridine, bipyridyl, 1,10-phenanthroline, methylcyanide) and through sulphur in the other adducts (formamide, dimethylformamide, acetamide, benzamide, acetanilide, triethylamine, aniline, *o*-, *m*-, *p*-toluidine, dimethyl aniline, urea, thiourea, DMSO).

INTRODUCTION

Literature survey reveals the formation of few stable adducts by antimony trichloride which is hygroscopic and unstable.[1, 2] Anhydrous antimony trichloride is soluble in benzene, chloroform, DMF, DMSO, THF etc. On careful evaporation of the amide solutions adducts of antimony trichloride are obtained. The solution of antimony trichloride react with O-, N-, S- donor Lewis bases to give adducts. These adducts on treatment with KCNS in THF form the trithiocyanato adducts of antimony(III). All the adducts of $SbCl_3$ are either white or light coloured solids and stable in dry atmosphere. The study is important from the point of view of the catalytic activity of antimony trichloride in a number of organic reactions.

Preparation of (antimony trithiocyanate) naphthalene adduct

1.50 g antimony trichloride-naphthalene adduct was dissolved in 50 mL dry THF and 1.50 g KCNS was added to it with shaking. The reaction mixture was kept for two days. The orange mother liquor was decanted off and evaporated to dryness leaving behind an orange solid. The solid was recrystallised from THF-ether mixture. Its analysis corresponded to $2Sb(NCS)_3 \cdot C_{10}H_8$.

If the thiocyanate reagent is taken in half the above amount and the reaction mixture is refluxed for 5 h, a deep orange mother liquor is obtained. The mother liquor on evaporation to dryness gave an orange red solid which was recrystallized with THF-ether mixture. The analysis of the solid corresponded to $Sb(SCN)_3 \cdot C_{10}H_8$.

The same procedures were used for other Lewis base adducts. N, N′-Dimethyl aniline, DMF, bipyridyl, 1,10-phenanthroline, and methyl cyanide formed 1 : 1 adduct, while others formed 1 : 2 adducts. With aniline adduct in hot solution the thiocyanate reaction produces 1 : 1 adduct, one molecule of aniline is knocked out.

The sulphur bonded thiocyanate adducts are darker in colour (deep orange to brown), while the nitrogen bonded thiocyanate adducts are lighter in colour (off white to yellow). The isothiocyanate adducts slowly change into thiocyanato ones on keeping (*ca.* 15 days) indicating more stability of the latter ones. The compounds decompose on heating, are hydrolysed by hot dilute acids and alkalies. Their analytical data and other physical characteristics are given in Table-1.

RESULTS AND DISCUSSIONS

The magnetic susceptibilities were measured by Guoy's method at 292 K using hydrated copper sulphate as the calibrant. The values are low (*ca.* 0.02–0.03 BM) indicating that they are all diamagnetic. The molar conductance measured on Leeds and Northrup type 4959 electrolytic conductivity bridge are very low (0.30–1.5 ohm^{-1} cm^2 mol^{-1}) indicating that they are essentially non-ionic. Cryoscopically determined molecular weights of the compounds pointed to their monomeric nature.

The IR absorption peaks in the aromatic hydrocarbon adducts are assigned as: ν(C—H) at *ca.* 3100 and 2900 cm^{-1}; π(C—H) in the region 850–730 cm^{-1} (naphthalene), two bands at 875 and 730 cm^{-1} (anthracene) and in the range 900–640 cm^{-1} (phenanthrene); δ(C—H) in the region 1250–950 cm^{-1} (naphthalene), two bands at 1150 and 1050 cm^{-1} (anthracene) and in the range 1500–900 cm^{-1} (phenanthrene). The peaks at *ca.* 1650, 1430 and 1380 cm^{-1} along with the decrease in C—C skeletal mode suggest that the bonding between antimony and the hydrocarbon molecule is through π-electrons[1,3]. The ν(C—N) appears[4] at *ca.* 2040 cm^{-1}, ν(C—S) in the region[5–7] 850–770 cm^{-1}, δ(NCS) at *ca.* 475 cm^{-1}, ν(Sb—N)[8] at *ca.* 450 cm^{-1}. Absence of bands for (Sb—S) bond, the high intensities of the band at *ca.* 2050 cm^{-1} and above observations suggest that all the thiocyanate groups are nitrogen bonded.

The assignment of bands in the aniline, *o*–, *m*–, and *p*-toluidine compounds are: ν_{asym}(N—H) *ca.* 3400, ν_{sym}(N—H) *ca.* 3360, δ(N—H) *ca.* 1600, ρ_t(N—H) *ca.* 1060 and ρ_w(N—H) *ca.* 520 cm^{-1}. ν(C—N) bands appear at *ca.* 1320 and 1210 cm^{-1} somewhat lowered due to (Sb—N) bonding[9]. A strong band at *ca.* 2090 cm^{-1} and medium to weak bands at *ca.* 710 and 420 cm^{-1} are assigned to ν(C—N), ν(C—S) and δ(NCS) respectively indicating sulphur bonded thiocyanate group to antimony[10]. The ν(Sb—S) are assigned at *ca.* 400 and 190 cm^{-1}.

The IR spectra of N, N′-dimethyl aniline and triethylamine compounds showed no ν(N—H) and δ(N—H) bands. The ν(C—N) appeared at 1330 and 1200 cm^{-1} in N, N′-dimethylaniline compound and at 1190 and 1080 cm^{-1} in triethylamine compound. The lowering of this frequency indicates the amine bonding through nitrogen. A strong band at *ca.* 2090 cm^{-1} is assigned to ν(C—N) and at *ca.* 710 and 415 cm^{-1} are due to ν(C—S) and δ(NCS) respectively indicating sulphur bonded thiocyanate group to antimony in both these compounds.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE ANTIMONY TRITHIOCYANATE ADDUCTS

Compound (ligand used)	Colour (Dec. temp.) (°C)	Mol. wt. Found (Calcd.)	Elemental analysis (%), Found (Calcd.)			Molar cond. (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
			Sb	N	S		
$2Sb(NCS)_3 \cdot C_{10}H_8$ (Naphthalene, cold)	Orange (98)	714.3 (719.0)	33.55 (33.80)	11.74 (11.68)	25.89 (26.70)	0.39	0.027
$Sb(NCS)_3 \cdot C_{10}H_8$ (Naphthalene, hot)	Orange red (102)	421.5 (423.5)	27.26 (28.69)	9.80 (9.92)	22.60 (22.67)	0.41	0.025
$2Sb(NCS)_3 \cdot C_{14}H_{10}$ (Anthracene, cold)	Yellow (110)	764.2 (769.0)	32.20 (31.60)	10.82 (10.92)	24.52 (24.97)	0.54	0.023
$Sb(NCS)_3 \cdot C_{14}H_{10}$ (Anthracene, hot)	Yellow (126)	470.0 (473.5)	25.32 (25.66)	8.84 (8.87)	20.29 (20.27)	0.61	0.024
$2Sb(NCS)_3 \cdot C_{14}H_{10}$ (Phenanthrene, cold)	Yellow (108)	764.0 (769.0)	32.11 (31.60)	10.95 (10.92)	24.90 (24.97)	0.58	0.025
$Sb(NCS)_3 \cdot C_{14}H_{10}$ (Phenanthrene, hot)	Yellow (123)	471.2 (473.5)	25.60 (25.66)	8.74 (8.87)	19.98 (20.27)	0.60	0.023
$Sb(SCN)_3 \cdot 2C_6H_5NH_2$ (Aniline, cold)	Brick red (83)	483.2 (481.5)	25.77 (25.23)	14.23 (14.54)	19.97 (19.94)	0.47	0.024
$Sb(SCN)_3 \cdot C_6H_5NH_2$ (Aniline, hot)	Red (87)	385.7 (388.5)	31.09 (31.27)	14.37 (14.41)	24.82 (24.71)	0.45	0.027

Compound (ligand used)	Colour (Dec. temp.) (°C)	Mol. wt. Found (Calcd.)	Elemental analysis (%), Found (Calcd.)			Molar cond. (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
			Sb	N	S		
$Sb(SCN)_3 \cdot 2CH_3C_6H_4NH_2$ (*o*-Toluidine)	Yellew (109)	507.2 (509.5)	23.78 (23.85)	13.80 (13.74)	18.72 (18.84)	0.53	0.028
$Sb(SCN)_3 \cdot 2CH_3C_6H_4NH_2$ (*m*-Toluidine)	Yellow (103)	504.3 (509.5)	23.73 (23.85)	13.60 (13.74)	18.56 (18.84)	0.56	0.022
$Sb(SCN)_3 \cdot 2CH_3C_6H_4NH_2$ (*p*-Toluidine)	Yellow (103)	505.6 (509.5)	23.64 (23.85)	13.82 (13.74)	18.78 (18.84)	0.52	0.026
$Sb(SCN)_3 \cdot C_6H_5N(CH_3)_2$ (N, N′-Dimethylaniline)	Dark green (117)	413.2 (416.2)	28.51 (29.17)	13.40 (13.44)	23.25 (23.05)	0.46	0.023
$Sb(SCN)_3 \cdot 2N(C_2H_5)_3$ (Triethylamine)	Red brown (101)	493.0 (497.5)	24.33 (24.42)	13.90 (14.07)	19.33 (19.30)	0.95	0.028
$Sb(SCN)_3 \cdot 2HCONH_2$ (Formamide)	Yellow (83)	387.8 (385.5)	31.08 (31.52)	18.01 (18.16)	24.96 (24.90)	1.12	0.027
$Sb(SCN)_3 \cdot HCON(CH_3)_2$ (N, N′-Dimethyl formamide)	Yellow (89)	366.2 (368.5)	32.90 (32.97)	15.29 (15.20)	26.25 (26.05)	1.25	0.022
$Sb(SCN)_3 \cdot 2CH_3CONH_2$ (Acetamide)	Red (85)	411.2 (413.5)	29.60 (29.38)	16.90 (16.93)	23.17 (23.22)	1.09	0.024
$Sb(SCN)_3 \cdot 2C_6H_5CONH_2$ (Benzamide)	Yellow (80)	539.0 (537.5)	22.90 (22.60)	13.00 (13.02)	17.80 (17.86)	0.72	0.024

Compound (ligand used)	Colour (Dec. temp.) (°C)	Mol. wt. Found (Calcd.)	Elemental analysis (%), Found (Calcd.)			Molar cond. (ohm^{-1} cm^{2} mol^{-1})	μ_{eff} (B.M.)
			Sb	N	S		
$Sb(SCN)_3 \cdot 2C_6H_5NHCOCH_3$ (Acetanilide)	Red (84)	560.1 (565.5)	21.42 (21.48)	12.25 (12.38)	17.02 (16.98)	0.64	0.025
$Sb(SCN)_3 \cdot 2NH_2CSNH_2$ (Thiourea)	Yellow (73)	444.8 (447.5)	27.01 (27.15)	21.34 (21.90)	35.42 (35.75)	0.98	0.023
$Sb(SCN)_3 \cdot 2NH_2CONH_2$ (Urea)	Yellow (63)	411.1 (415.5)	29.03 (29.24)	23.43 (23.59)	22.92 (23.10)	1.15	0.022
$Sb(SCN)_3 \cdot 2(CH_3)_2SO$ (Dimethyl sulphoxide)	Yellow (74)	454.5 (451.5)	27.10 (26.91)	9.18 (9.30)	35.23 (35.44)	0.97	0.024
$Sb(NCS)_3 \cdot CH_3CN$ (Methyl cyanide)	Brick red (105)	334.8 (336.5)	35.89 (36.11)	16.52 (16.64)	28.25 (28.53)	1.11	0.023
$Sb(NCS)_3 \cdot 2C_5H_5N$ (Pyridine)	Orange (123)	450.7 (453.5)	26.52 (26.79)	15.31 (15.43)	21.01 (21.17)	0.53	0.027
$Sb(NCS)_3 \cdot C_{10}H_8N_2$ (2, 2′-Bipyridyl)	Yellow (125)	454.9 (451.5)	26.49 (26.91)	15.68 (15.50)	21.10 (21.26)	0.44	0.025
$Sb(NCS)_3 \cdot C_{12}H_8N_2$ (1,10-Phenanthroline)	Yellow (129)	472.8 (475.5)	25.72 (25.55)	14.64 (14.72)	20.25 (20.19)	0.63	0.025

The IR spectra of the thiocyanato compounds with formamide, acetamide, benzamide, acetanilide and urea showed absorption bands at *ca.* 3410 and 3300 cm^{-1} due to $\nu_{asym}(N—H)$ and $\nu_{sym}(N—H)$ respectively. The $\delta(N—H)$ band is assigned at *ca.* 1610 cm^{-1}. The dimethyl formamide compound IR spectra did not show these bands. The $\nu(C{=}O)$ band is assigned at *ca.* 1610 cm^{-1}; the lowering of this band as compared to the free ligands indicated that all the amides are oxygen bonded to antimony[11]. A band at *ca.* 1390 cm^{-1} is assigned to $\nu(C—N)$ but in acetanilide it appears at 1280 cm^{-1} and is considered as a mixed band due to $\nu(CN)$, $\delta(N—H)$ and $\nu(CH_3—C)$.[12] The $\nu(Sb—O)$ appeared in the range 450–400 cm^{-1} in the IR spectra of these compounds.[8] The presence of a strong band at *ca.* 2080 cm^{-1} is due to $\nu(CN)$, *ca.* 710 cm^{-1} due to $\nu(C—S)$ and *ca.* 410 cm^{-1} is due to $\delta(NCS)$ which overlaps with $\nu(Sb—O)$, $\nu(Sb—N)$ and $\nu(Sb—S)$ appearing between the range 460–400 cm^{-1}. Sulphur bonded thiocyanate groups are present in these compounds. In the thiourea-thiocyanate complex the IR assignments are; $\nu_{asym}(N—H)$ at 3450, 3310 cm^{-1}, $\nu_{sym}(N—H)$ at 3240 cm^{-1}, the bands at 1640, 1460, 1420 and 1010 cm^{-1} may be composite bands for $\delta(NH_2)$, $\nu(C—N)$ and $\nu(C{=}S)$. The lowering of the last frequency from 1086 cm^{-1} to 1010 cm^{-1} indicated the coordination of thiourea to antimony through sulphur atom[13]. The band at 670 cm^{-1} may be assigned to $\nu(C{=}S)$ with some contributions from $\delta(NCS)$. The $\nu(C—N)$ to 1380 cm^{-1} and the lowering of $\nu(C{=}S)$ from 730 to 670 cm^{-1} supports coordination of thiourea molecules through sulphur[14]. A strong band at 2085 cm^{-1} is due to $\nu(C—N)$, 710 cm^{-1} due to $\nu(C—S)$ and 410 cm^{-1} is due to $\delta(NCS)$ respectively which overlaps with $\nu(Sb—S)$ occurring in the range 390–170 cm^{-1}. These observations indicate the sulphur bonded thiocyanate group in the compounds.

The dimethylsulphoxide thiocyanate compound showed $\nu_{asym}(C—H)$ at 2950 cm^{-1}, $\nu_{sym}(C—H)$ at 2860 cm^{-1}, $\delta(CH_3)$ at 1360 and 1320 cm^{-1} and $\rho(CH_3)$ at 930 and 910 cm^{-1}. The lowering of $\nu(S{=}O)$ from 1100 cm^{-1} to 960 cm^{-1} indicated the coordination of the sulphoxide molecules through oxygen atom. Presence of a strong band at 2085 cm^{-1} is assigned to $\nu(C—N)$, a band at 715 cm^{-1} to $\nu(C—S)$ and at 410 cm^{-1} to $\delta(NCS)$ which overlaps with $\nu(Sb—O)$ and $\nu(Sb—S)$ which are assigned at 390 and 180 cm^{-1} respectively. This is indicative of the sulphur bonded thiocyanate group in the compound.

The IR spectra of methyl cyanide compound showed $\nu_{asym}(C—H)$ at 2990 cm^{-1}, $\nu_{sym}(C—H)$ at 2870 cm^{-1}, $\nu_{asym}(CH_3)$ at 1460 cm^{-1}, $\nu_{sym}(CH_3)$ at 1360 cm^{-1}, $\rho_r(CH_3)$ at 960 and 910 cm^{-1}. $\nu(C—N)$ is assigned at 2290 cm^{-1} which is on the higher side pointing the nitrogen coordination of CH_3CN to antimony. A strong band at 2040 cm^{-1} is due to $\nu(C—N)$ of the NCS group, 830 cm^{-1} due to $\nu_{sym}(C—S)$ and a band at 460 cm^{-1} is assigned to $\delta(NCS)$; while $\nu(Sb—N)$ appeared at 345 cm^{-1}.

The IR spectra of pyridine, 2-2′-bipyridyl and 1,10-phenanthroline compounds showed a strong band at *ca.* 2040 cm^{-1} assigned to $\nu(C—N)$, at *ca.* 840 cm^{-1} due to $\nu(C—S)$ and at *ca.* 480 cm^{-1} due to $\delta(NCS)$ respectively suggesting the nitrogen coördination of the thiocyanate group to antimony. The $\nu(Sb—N)$ appeared between 390-350 cm^{-1}, the δ-(ring) and π-(ring) are assigned at *ca.* 660 and 480 cm^{-1} respectively which are on the higher side, indicating coördination of pyridine and others to antimony. The high frequency region frequencies for ν-(ring), ν(C—H), δ(C—H) and π(C—H) are not shifted appreciably.

The electronic spectra of the compounds show two bands in the region *ca.* 315 and 260 nm with E_{max} *ca.* 12100. These bands could be assigned to charge transfer bands[15].

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