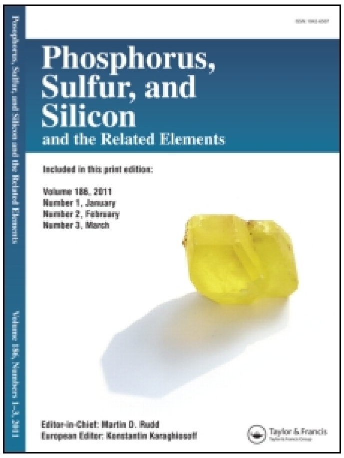

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF MIXED N-(SALICYLIDENE)-o-MERCAPTOANILINE DIALKYLDITHIOPHOSPHATO DERIVATIVES OF ANTIMONY(III)

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Mixed N-(salicylidene)-o-mercaptoaniline dialkyldithiophasphato derivatives of antimony(III) were synthesized by the substitution reactions of chlorobis [N-(salicylidene)-o-mercaptoaniline] antimony(III), $Sb[SC_6H_4N=C(H)C_6H_4OH]_2Cl$; dichloro [N-(salicylidene)-o-mercaptoaniline] antimony(III), $Sb[SC_6H_4N=C(H)C_6H_4OH]Cl_2$ and monochloro [N-(salicylidene)-o-mercaptoaniline]antimony(III), $\overline{Sb[SC_6H_4N=C(H)C_6H_4O]}Cl$ with the ammonium salt of dialkyldithiophosphates in 1:1, 1:2 and 1:1 molar ratios, respectively, in benzene. These yellow or orange crystalline complexes have been characterized by elemental analysis, melting points, molecular weight measurements and spectroscopic (IR, ^1H, ^{13}C and ^{31}P NMR) studies.

Keywords: N-(salicylidene)-o-mercaptoaniline; dialkyldithiophosphate; antimony trichloride; pharmacological; bidentate; distorted octahedral; molecular weights

Complexes of non-transition metals with Schiff bases containing sulfur and nitrogen as donor atoms have been extensively studied due to their pharmacological and technical uses[1,2] in the last decade. The studies on dithio and Schiff base complexes of group VA elements were confined to mixed halide dithio[3–6]and mixed halide Schiff base complexes. Considerable emphasis has recently been placed on the synthesis of antimony(III) complexes in mixed environment i.e. hard and soft ligands in the co-ordination sphere[7–9]. However in many cases the steric blockade may substan-

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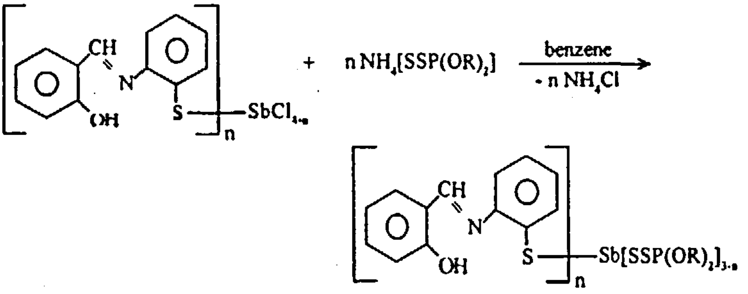
* Corresponding author.

tially modify the reactivity at the antimony(III) center. Thus based on the pharmacological, technical and kinetic importance of mixed ligand complexes, we report herein some new mixed ligand "N-(salicylidene)-o-mercaptoaniline dialkyldithiophosphato derivatives of antimony (III).

RESULTS AND DISCUSSION

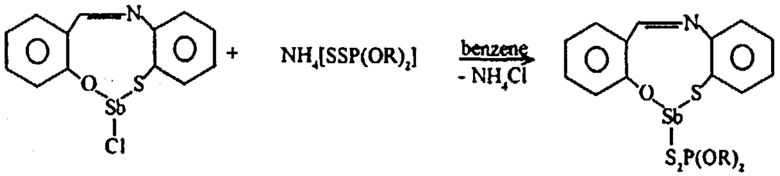
The dichloro, chlorobis and monochloro [N-(salicylidene)-o-mercaptoaniline] antimony(III) complexes, which were prepared by the reactions of antimony trichloride with the sodium salt of N-(salicylidene)-o-mercaptoaniline in 1:1, 1:2 and 1:1 molar ratios, respectively in benzene[10], were used as starting materials for the preparation of mixed ligand complexes of antimony (III).

Mixed ligand complexes were synthesized by reacting the chlorobis and dichloro [N-(salicylidene)-o-mercaptoaniline] antimony(III) complexes with the ammonium salt of dialkyldithiophospates in 1:1 and 1:2 molar ratios, respectively, in benzene.



Where, n = 1,2; R = Et, *i*-Pr, *i*-Bu

Similarly, the mixed derivatives of monochloro [N-(salicylidene)-o-mercaptoaniline] antimony(III) were synthesized with the ammonium salt of dialkyldithiophosphates in 1:1 molar ratio.



Where, R = Et, *i*-Pr, *i*-Bu

Infrared Spectral Data

Characteristic bands in the IR spectra of the present mixed ligand complexes have been assigned by comparison with the spectra of the corresponding tris-(dialkyldithiophosphate) antimony(III)[6] and tris[N-(salicylidene)-o-mercaptoaniline] antimony(III)[10] complexes. The bands in the regions 1030–960 cm^{-1} and 880–730 cm^{-1} are assigned to (P)-O-C and P-O-(C) stretching modes respectively[6]. A strong band, observed in the region 680–620 cm^{-1} due to v(P=S)[12] in the spectra of the dialkyldithiophosphoric acids and their ammonium salt, is shifted to lower frequencies (by ~ 30 cm^{-1}) in the corresponding antimony(III) derivatives. This probably indicates a strong bidentate chelation of the ligand with antimony[6]. IR studies on tris [N-(salicylidene)-o-mercaptoaniline] antimony(III) showed that occurrence of a band at 1590 cm^{-1} due to v(C=N) (azomethine) and at 330 cm^{-1} due to v(Sb-S) could be taken as an indication of the bidentate nature of the N-(salicylidene)-o-mercaptoaniline moiety[10].

Nuclear Magnetic Resonance Spectral Data

The ^1H NMR spectra of these complexes in $CDCl_3$ show characteristic resonances due to alkoxy and phenylprotons (Table III). A singlet, observed at δ 3.10–3.60 ppm in the parent dithio acid and assigned for the SH proton, is found to be absent in the spectra of the corresponding mixed ligand antimony(III) complexes indicating deprotonation of SH group and formation of Sb-S bond[13]. The ethyl protons exhibit a triplet at δ 1.40 ppm due to CH_3 protons and a quartet at δ 4.25 ppm due to $-OCH_2$protons. The isopropyl protons appear as a doublet at δ 1.65 ppm due to CH_3 protons and a multiplet centered at δ4.75 ppm due to -OCH protons. The isobutyl protons appear as a doublet at δ 0.98 ppm due to CH_3 protons, a multiplet centered at δ 1.95 ppm due to CH protons and a doublet at δ 3.90 ppm due to $-OCH_2$ protons. A multiplet of phenyl protons is present in the region δ 6.80–8.10 ppm.

^{13}C NMR spectra of few representative compounds of antimony(III) derivatives have been recorded. There is no significant chemical shift for the various ^{13}C signals present in the mixed ligand complexes of antimony(III) as compared to the corresponding tris (dialkyldithiophosphate) antimony(III) and tris[N-(salicylidene)-o-mercaptoaniline] antimony(III)[10] complexes.

TABLE I Reactions between chloroderivatives of [N-(salicylidene)-o-mercaptoaniline] antimony(III) and dialkyldithiophosphates in different stoichiometric ratios

S.No.	*Reactants*		*Molar ratio*	*Product (g)*	*Yield (%)*	*M.p. (°C)*	*Mol. Wt. f(c)*	*Analysis: % found (calcd.)*				
	Complex	*Ligand*						*C*	*H*	*Sb*	*N*	*S*
1.	$[L]_2SbCl$	$H_4NSSP(OC_2H_5)_2$	1:1	$[L]_2Sb[SSP(OC_2H_5)_2]$	86	96	760	47.00	3.87	15.94	3.76	16.34
	(1.78)	(0.75)		(2.28)			(762.99)	(47.18)	(3.93)	(15.95)	(3.66)	(16.77)
2.	$[L]SbCl_2$	$H_4NSSP(OC_2H_5)_2$	1:2	$[L]Sb[SSP(OC_2H_5)_2]_2$	88	99	722	34.84	4.01	16.72	1.87	22.01
	(0.95)	(0.90)		(1.40)			(719.87)	(35.00)	(4.16)	(16.91)	(1.94)	(22.22)
3.	$[L']SbCl$	$H_4NSSP(OC_2H_5)_2$	1:1	$[L']_2Sb[SSP(OC_2H_5)_2]$	90	107	610	32.12	3.22	21.12	3.34	15.83
	(1.50)	(0.79)		(1.72)			(604.87)	(33.72)	(3.14)	(20.12)	(2.31)	(15.87)
4.	$[L]_2SbCl$	$H_4NSSP(OC_3H_7)_2$	1:1	$[L]_2Sb[S\ SP(OC_3H_7)_2]$	90	96	796	48.41	4.21	15.18	3.44	16.00
	(1.60)	(0.60)		(1.65)			(791.20)	(48.53)	(4.29)	(15.38)	(3.53)	(16.17)
5.	$[L]SbCl_2$	$H_4NSSP(OC_3H_7)_2$	1:2	$[L]Sb[SSP(OC_3H_7)_2]$	89	106	763	37.98	4.66	15.54	1.71	20.42
	(0.90)	(0.99)		(1.63)			(779.39)	(38.49)	(4.87)	(15.62)	(1.79)	(20.53)
6.	$[L']SbCl$	$H_4NSSP(OC_3H_7)_2$	1:1	$[L']Sb[SSP(OC_3H_7)_2]$	78	111	560	39.76	3.88	20.94	2.36	17.14
	(1.40)	(0.84)		(1.92)			(563.08)	(40.49)	(4.08)	(21.62)	(2.48)	(17.04)
7.	$[L]_2SbCl$	$H_4NSSP(OC_4H_9)_2$	1:1	$[L]_2Sb[SSP(OC_4H_9)_2]$	79	102	819	48.11	4.33	14.45	3.21	15.32
	(1.55)	(0.68)		(1.70)			(828.18)	(49.26)	(4.58)	(14.70)	(3.38)	(15.45)
8.	$[L]SbCl_2$	$H_4NSSP(OC_4H_9)_2$	1:2	$[L]Sb[SSP(OC_4H_9)_2]_2$	84	107	864	39.22	5.11	14.06	1.76	18.77
	(0.81)	(1.02)		(1.43)			(850.26)	(40.92)	(5.41)	(14.31)	(1.64)	(18.81)
9.	$[L']SbCl$	$H_4NSSP(OC_4H_9)_2$	1:1	$[L']Sb[SSP(OC_4H_9)_2]$	85	110	601	41.26	4.44	20.09	2.22	15.88
	(1.36)	(0.94)		(1.63)			(599.06)	(42.06)	(4.50)	(20.32)	(2.33)	(16.02)

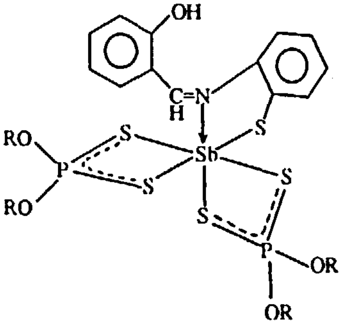
$L = [HOC_6H_4\ C(H){=}N\ C_6H_4S]$- ; $L' = $ -$[OC_6H_4C(H){=}N\ C_6H_4S]$-

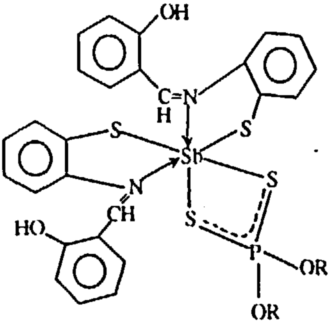
TABLE II Infrared spectral data of mixed ligand complexes of antimony(III)

S.No.	*Compound*	*IR (cm^{-1})*						
		v(OH)	*v(C=N)*	*v(Sb-S)*	*v(P)-O-C*	*vP-O-(C)*	*v(P=S)*	*v(C=S)*
1.	$[(C_2H_5O)_2PSS]_2\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]$	3250	1610	330	980	895	670	560
2.	$[(C_2H_5O)_2PSS]\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	3050	1600	325	995	850	695	520
3.	$[(C_2H_5O)_2PSS]\text{-}\overline{\text{Sb-}[SC_6H_4N{=}C(H)C_6H_4O}]$	--	1595	335	990	790	700	540
4.	$[(i\text{-}C_3H_7O)_2PSS]_2\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]$	3320	1590	320	1030	770	690	535
5.	$[(i\text{-}C_3H_7O)_2PSS]\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	3015	1620	328	1020	890	685	530
6.	$[(i\text{-}C_3H_7O)_2PSS]\text{-}\overline{\text{Sb-}[SC_6H_4N{=}C(H)C_6H_4O}]$	--	1590	330	1015	795	690	520
7.	$[(i\text{-}C_4H_9O)_2PSS]_2\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]$	2960	1605	340	1005	880	700	515
8.	$[(i\text{-}C_4H_9O)_2PSS]\text{-Sb-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	3180	1585	335	995	830	710	530
9.	$[(i\text{-}C_4H_9O)_2PSS]\text{-}\overline{\text{Sb-}[SC_6H_4N{=}C(H)C_6H_4O}]$	--	1590	328	1020	820	690	540

Proton coupled decoupled ^{13}P NMR spectra of these complexes could be obtained (Table III). In proton decoupled spectra only one peak for each compound in the range of 92.1–93.8 ppm is obtained. The ^{31}P chemical shift values observed in the parent dialkyldithiophosphoric acids are shifted towards downfield in the corresponding antimony(III) complexes (by 10–15 ppm). This indicates the bidentate behavior of the dialkyldithiophosphate moiety[14,15] in all these derivatives which is further supported by the IR spectral data.

The above studies indicate a bidentate mode of attachment of the both types of ligands to the metal atom. The central antimony atom appears to acquire the coordination number five and six. The most plausible geometry for these complexes appears to be distorted octahedral if the presence of the stereochemically active lone pair is also considered in the coordination sphere with pseudo six and seven coordinated structures.





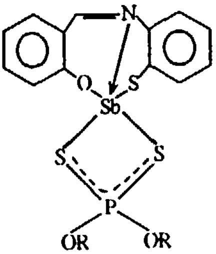


TABLE III NMR spectral data of mixed ligand complexes of Antimoriy(III)

S.No.	Compound	^1H NMR (δ ppm)	^{31}P (δ ppm)		
			Chemical shifts proton decoupled	Chemical shifts proton coupled	Coupling constant ^3J (POCH)
1.	$[(C_2H_5O)_2PSS]_2\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]$	6.70–8.0, m, 8H (Ph); 3.95, s, 1H (=CH); 1.40, t, 12H, (CH_3) ; 4.25, q, 8H (OCH_2).	92.4	--	--
2.	$[(C_2H_5O)_2PSS]\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	6.80–8.10, m 16H (Ph); 4.0, s, 2H (=CH); 1.48, t, 6H (CH_3) ; 4.32, q, 4H (OCH_2).	90.2	--	--
3.	$[(C_2H_5O)_2PSS]\text{-}\overline{Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4O}]$	7.0–8.10, m, 8H (Ph); 3.90, s, 1H (=CH); 1.45, t, 6H (CH_3) ; 4.40, q, 4H (OCH_2).	93.0	--	--
4.	$[(i\text{-}C_3H_7O)_2PSS]_2\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]$	6.85–7.90, m, 8H (Ph); 3.82, s, 1H (=CH); 1.65, d, 24H (CH_3) ; 4.75, m, 4H (OCH).	92.1	--	--
5.	$[(i\text{-}C_3H_7O)_2PSS]\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	6.95–8.0, m 16H (Ph); 4.10, s, 2H (=CH); 1.60, d, 12H (CH_3) ; 4.90, m, 2H (OCH).	93.2	--	--
6.	$[(i\text{-}C_3H_7O)_2PSS]\text{-}\overline{Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4O}]$	7.10–8.20, m, 8H (Ph); 4.12, s, 1H (=CH); 1.72, d, 12H (CH_3) ; 4.95, m, 2H (OCH).	91.0	--	--

S.No.	*Compound*	*^1H NMR (δ ppm)*	*^{31}P (δ ppm)*		
			Chemical shifts proton decoupled	*Chemical shifts proton coupled*	*Coupling constant ^3J (POCH)*
7.	$[(i\text{-}C_4H_9O)_2PSS]_2\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]$	6.75–7.92, m, 8H (Ph); 3.80, s, 1H (=CH); 0.95, d, 24H (CH_3);1.95, m, 4H (CH); 3.90, d, 8H (OCH_2).	93.8	3967.4– 4002.8 Hz 5 peaks	8.85 Hz
8.	$[(i\text{-}C_4H_9O)_2PSS]\text{-}Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4OH]_2$	6.98–8,0, m, 16H (Ph); 3.78, s, 2H (=CH); 0.98, d, 12H (CH_3) ; 1.98, m, 2H (CH); 3.92, d, 4H (OCH_2).	91.9	4031– 4067 Hz 5 peaks	8.84 Hz
9.	$[(i\text{-}C_4H_9O)_2PSS]\text{-}\overline{Sb\text{-}[SC_6H_4N{=}C(H)C_6H_4O}]$	7.0–8.12, m, 8H (Ph); 3.92, s, 1H (=CH); 1.02, d, 12H (CH_3) ; 1.92, m, 2H (CH), 3.90, d, 4H (OCH_2).	92.6	3995.6– 4033 Hz 5 peaks	8.97 Hz

EXPERIMENTAL

All the experiments were carried out in moisture free atmosphere. Solvents were dried by standard methods[16]. Antimony trichloride was distilled under reduced pressure before use. N-(salicylidene)-o-mercaptoaniline[17] and dialkyldithiophosphoric acids[18–20] and their ammonium[19] salts were prepared by previously reported methods. Sulfur was estimated gravimetrically as barium sulfate, nitrogen was estimated by Kjeldahl's method[21] and antimony was estimated iodometrically[22] after converting Sb(III) to Sb(V) by heating with $KMnO_4$, excess $KMnO_4$ was decolorised by H_2O_2 and excess H_2O_2 was removed by evaporation. The remaining solid mass was dissolved in HCl, KI was added and liberated iodene was titrated against standard sodiumthiosulfate solution using starch as an internal indicator. The IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer. The ^1H NMR spectra were recorded on a Perkin-Elmer R-32 using TMS as an internal standard and ^{13}C NMR on JEOL FX-90 using TMS as an external standard and ^{31}P NMR spectra were recorded on JEOL FX-90 using H_3PO_4 as an external standard.

Chloro derivatives of [N-(salicylidene)-o-mercaptoaniline]] antimony (III) were synthesized as reported earlier[10].

TABLE IV ^{13}C NMR spectral data of some mixed ligand complexes of antimony(III) (δ ppm)

Compound No.	*- C_6H_5**	*HC=N*	*OCH_2*	*OCH*	*CH*	*CH_3*
2.	151.85; 150.42; 119.53; 119.47 132.77; 132.58; 121,52; 120.24 131.99; 129.03; 117.86; 116.78	157.90	47.43	----	----	15.93
3.	155.42; 153.24; 120.91; 119.22 133.32; 129.44; 122.42; 120.34 129,46; 128,40; 118.12; 117,46	160.00	48.22	----	----	16.25
5.	154.26; 147.22; 118.44; 119.12 132.69; 128.85; 121.59; 121.74 128.36; 128.18; 119.12; 115.49	158.34	----	64.78	----	18.05
6.	152.50; 151.06; 119.11; 118.46 132.20; 131.65; 123.78; 122.88 128.11; 128.01; 117.16; 116.05	159.20	----	66.24	----	18.42
7.	153.42; 151.24; 119.24; 119.32 132.62; 132.58; 121.44; 120.32 130.42; 129.20; 117.62; 116.66	151.92	47.41	----	28.74	18.85

* Values are in the order of C-1, C-1′, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′, C-6, C-6′.

Synthesis of mixed ligand complexes of antimony(III)

The mixed ligand complexes of antimony(III) were synthesized by the substitution reaction of [N-(salicylidene)-o-mercaptoaniline] antimony(III) derivatives with the ammonium salt of dialkyl dithiophosphates in different stoichiometric ratios.

Reaction between chlorobis [N-(salicylidene)o-mercaptoaniline] antimony(III) and ammonium salt of diethyl dithiophosphate in 1:1 molar ratio

The chlorobis [N-(salicylidene)]-o-mercaptoaniline antimony(III) (1.78g, 2.3 mmole) and ammonium salt of diethyldithiophosphate (0.75g, 2.3 mmole) were mixed in 1:1 ratio in dry benzene and stirred with heating in an oil bath for about two hours. Precipitated ammonium chloride was removed by filtration, followed by removal of the solvent giving the desired product (yield 2.28 g). These yellow solids were crystallised from benzene-petroleum ether (40–60°) mixture.

All the other mixed N-(salicylidene)-o-mercaptoaniline dialkyldithiophosphate derivatives of antimony(III) were synthesised in the same route. The pertinent data of these complexes listed in table I .

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