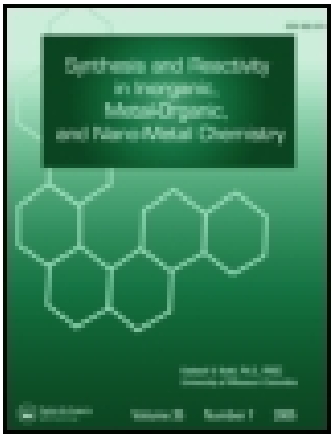

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Synthesis and Spectroscopic Sit Dies of Mixed Benziedioximate. Dialkyl Dithiophosphato Derivatives of Antimony (III)

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF MIXED BENZILDIOXIMATE DIALKYL DITHIOPHOSPHATO DERIVATIVES OF ANTIMONY(III)

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ABSTRACT

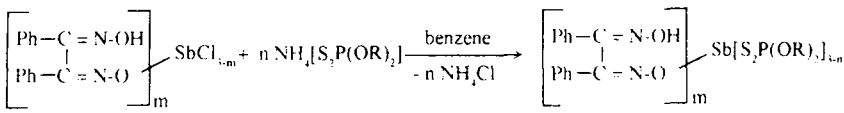
Replacement reactions of chloroderivatives of (benzildioximato)antimony(III) with dialkyl dithiophosphates in different stoichiometric ratios in benzene yield mixed ligand derivatives, benzildioximatoantimony(III) dialkyl dithiophosphates. The yellow coloured compounds have been characterized by elemental analyses, molecular weight measurements and spectroscopic (IR, ^{1}H, ^{13}C and ^{31}P NMR) studies.

INTRODUCTION

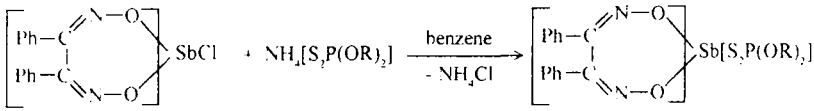
Much literature is available on dialkyl dithiophosphates[1-3] as well as oximates[4,5] of antimony(III). However, comparatively less attention has been paid to mixed dialkyl dithiophosphate complexes of antimony(III)[6]. Chelates of antimony(III) moieties with N, O and S donor ligands have been received much attention during the last few years[7,8] Oxime derivatives of antimony(III) have attracted the attention of chemists in the recent past In view of the fascinating structures[9], bonding characteristics[10], and potential applicability[11] of antimony(III) complexes, we report in the present paper the synthesis and characterization of some mixed benzildioximate dialkyl dithiophosphato complexes of antimony(III).

RESULTS AND DISCUSSION

The mixed ligand derivatives of antimony(III) have been synthesized by the reaction of chlorobis, dichloro and monochloro antimony(III) derivatives of benzildioxime with the ammonium salt of dialkyl dithiophosphates in 1:1, 1:2 and 1:1 molar ratios, respectively, in benzene The chloro derivatives of benzildioximatoantimony(III) have been synthesized and characterised in our laboratory[5].



Where m = 1, n = 2, R = Et, Compd. (1); m = 2, n = 1, R = Et, Compd. (2); m = 1, n = 2, R = i-Pr, Compd. (3); m = 2, n = 1, R = i-Pr, Compd. (4); m = 1, n = 2, R = i-Bu, Compd. (5); m = 2, n = 1, R = i-Bu, Compd. (6).



Where R = Et, Compd. (7); R = i-Pr, Compd. (8); R = i-Bu, Compd. (9).

These reactions were carried out by stirring the reactants in dry benzene with slight heating (45-50°C) for about 2-3 h. The complexes are yellow solids which are soluble in DMSO, DMF, $CHCl_3$, and benzene, and are monomeric in $CHCl_3$.

IR 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(benzildioximato)antimony(III)[5] and tris(dialkyl dithiophosphato)antimony(III)[3] complexes. Infrared spectra of the mixed ligand derivatives show a new band in the region 460-445 cm^{-1}, which can be attributed to the formation of an antimony-oxygen (Sb-O) bond[12]. A strong band at 1610 cm^{-1} due to ν(C=N) in the tris derivatives does not show any discernible shift in the spectra of the derivatives, indicating that the C=N group is not taking part in coordination. 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,[3] respectively. A strong band observed in the region 680-625 cm^{-1} due to ν(P=S)[13] in the spectra of dialkyl dithiophosphoric acids and their ammonium salts is shifted to lower frequencies by about 30 cm^{-1} in the mixed derivatives, and a strong band in the region 360-335 cm^{-1} due to ν(Sb-S) vibrations[14] indicates a strong bidentate chelation of the ligands with antimony.

NMR Spectral Data

The ^1H NMR spectra of the mixed ligand complexes in $CDCl_3$ show characteristic resonances due to alkoxy and phenyl protons (Table III). All of the mixed ligand complexes of antimony(III) show a multiplet due to the phenyl protons in the region δ 6.85-8.00 ppm. 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 1.60 ppm due to CH_3 protons and a multiplet centered at δ 4.70 ppm due to OCH protons. The

Table I. Reactions Between Chloroderivatives of (Benzildioximato)antimony(III) and Dialkyl Dithiophosphates in Different Stoichiometric Ratios

Compd No.	Reactants (g)		Molar ratio	Product Emp Form , (g)	Yield (%)	M p (°C)	Mol Wt f (c)	Analysis % found (calcd)				
	Complex	Ligand						C	H	Sb	N	S
(1)	$[L]SbCl_2$ (0 90)	$H_4N[S_2P(OC_2H_4)_2]$ (0 51)	1 2	$C_{22}H_{31}N_3O_6P_2S_4Sb$ (1 42)	88	121	780 (784 79)	48 11 (48 93)	2 44 (2 54)	15 45 (15 51)	7 02 (7 14)	08 00 (08 15)
(2)	$[L]_2SbCl$ (1 60)	$H_4N[S_2P(OC_2H_4)_2]$ (0 85)	1 1	$C_{33}H_{33}N_4O_6PS_2Sb$ (1 26)	76	118	732 (730 83)	35 77 (36 12)	4 12 (4 24)	16 50 (16 66)	3 70 (3 83)	17 41 (17.51)
(3)	$[L]SbCl_2$ (0 86)	$H_4N[S_2P(OC_2H_4)_2]$ (0 79)	1 2	$C_{26}H_{19}N_2O_6P_2S_4Sb$ (1 62)	77	116	550 (544 79)	39 12 (39 64)	3 56 (3 67)	22 62 (22 74)	5 01 (5 13)	11 70 (11 74)
(4)	$[L]_2SbCl$ (1.56)	$H_4N[S_2P(OC_3H_7)_2]$ (0 56)	1 1	$C_{54}H_{56}N_4O_6PS_2Sb$ (1 32)	84	118	802 (812.82)	49 82 (50 19)	2 84 (2 95)	14.62 (14 97)	6 28 (6 88)	7 55 (7 87)
(5)	$[L]SbCl_2$ (0 75)	$H_4N[S_2P(OC_3H_7)_2]$ (0 85)	1:2	$C_{30}H_{47}N_2O_6P_2S_4Sb$ (1 12)	83	119	794 (786 88)	38 88 (39 65)	4 22 (4 95)	15 12 (15 47)	3 42 (3 55)	16 00 (16 26)
(6)	$[L]_2SbCl$ (1 55)	$H_4N[S_2P(OC_3H_7)_2]$ (0 85)	1 1	$C_{36}H_{40}N_4O_6PS_2Sb$ (1 54)	80	122	558 (572 81)	40 21 (41 89)	4 10 (4 18)	20 82 (21 25)	4 52 (4 88)	11.21 (11 17)
(7)	$[L']SbCl$ (1 54)	$H_4N[S_2P(OC_4H_9)_2]$ (0 65)	1 1	$C_{18}H_{20}N_2O_4PS_2Sb$ (1 37)	70	125	855 (841)	51 21 (50 82)	3 01 (3 29)	13.82 (14 32)	6 08 (6 58)	07 12 (07 52)
(8)	$[L']SbCl$ (1.46)	$H_4N[S_2P(OC_4H_9)_2]$ (0 93)	1 2	$C_{20}H_{24}N_3O_4PS_2Sb$ (1 22)	91	115	856 (843)	40 86 (41 80)	5 50 (5 45)	14 15 (14 13)	3 39 (3 25)	14 16 (14 86)
(9)	$[L']SbCl$ (1.30)	$H_4N[S_2P(OC_4H_9)_2]$ (0 88)	1 1	$C_{37}H_{28}N_2O_4PS_2Sb$ (1 36)	87	120	567 (601)	46 76 (46 64)	4 77 (4 94)	20 91 (21 51)	4 80 (4 94)	11 22 (11 30)

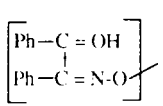
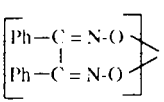
L =  and L' = 

Table II. Infrared Spectral Data of Mixed-Ligand Complexes of Antimony(III)

Comp No	Compound	IR (cm^{-1})					
		ν(C=N)	ν(Sb-O)	ν(Sb-S)	ν[(P)-O-C]	ν[P-O-(C)]	ν(P=S)
(1)	$[L]Sb[S_2P(OC_2H_5)_2]_2$	1590 v	465 sh	340 m	995 m	765m	690 sh
(2)	$[L]_2Sb[S_2P(OC_2H_5)_2]$	1598 v	470 sh	345 m	980 m	780 m	700 sh
(3)	$[L]Sb[S_2P(OC_3H_7)_2]_2$	1605 v	463 sh	335 m	1000 m	830 m	685 sh
(4)	$[L]_2Sb[S_2P(OC_3H_7)_2]$	1600 v	455 sh	342 m	1010 m	790 m	665 sh
(5)	$[L]Sb[S_2P(OC_4H_9)_2]_2$	1592 v	475 sh	340 m	992 m	860 m	692 sh
(6)	$[L]_2Sb[S_2P(OC_4H_9)_2]$	1615 v	470 sh	345 m	980 sh	880 m	715 sh
(7)	$[L']Sb[S_2P(OC_2H_5)_2]$	1592 v	472 sh	360 m	990 m	820 m	705 sh
(8)	$[L']Sb[S_2P(OC_3H_7)_2]$	1610 v	466 sh	340 m	986 sh	865 m	660 sh
(9)	$[L']Sb[S_2P(OC_4H_9)_2]$	1600 v	460 sh	335 m	998 m	795 m	690 sh

s = strong m = medium, v = variable, sh = sharp

Table III. NMR Spectral Data of Mixed-Ligand Complexes of Antimony(III)

Compd No.	Compound	^{1}H NMR (δ ppm)	^{31}P (δ ppm)		
			Chemical shifts, proton-decoupled	Chemical shifts, proton-coupled	Coupling constant ^{3}J(POCH)
(1)	$[L]Sb[S_2P(OC_2H_5)_2]_2$	7.0-7.95, m, 10H, Ph, 11.0, s, 1H, OH; 1.48, t, (J=7.1 Hz), 12H, CH_3, 4.65, q, (J=3.5 Hz), 8H, OCH_2.	91.8	–	–
(2)	$[L]_2Sb[S_2P(OC_2H_5)_2]$	7.05-8.00, m, 20H, Ph, 11.5, s, 2H, OH, 1.40, t, (J=7.1 Hz), 6H, CH_3, 4.60, q, (J=3.5 Hz), 4H, OCH_2.	91.6	–	–
(3)	$[L]Sb[S_2P(OC_3H_7)_2]_2$	6.90-7.95, m, 10H, Ph, 12.0, s, 1H, OH, 1.68, d, (J=7.1 Hz), 24H, CH_3, 4.90, m, 4H, OCH	90.9	–	–
(4)	$[L]_2Sb[S_2P(OC_3H_7)_2]$	7.0-8.1, m, 20H, Ph, 11.8, s, 1H, OH, 1.72, d, (J=7.1 Hz), 12H, CH_3; 4.82, m, 2H, OCH.	92.0	–	–
(5)	$[L]Sb[S_2P(OC_4H_9)_2]_2$	7.15-8.00, m, 10H, Ph, 11.0, s, 1H, OH; 1.05, d, (J=7.1 Hz), 24H, CH_3, 1.90, m, 4H, CH; 3.95, d, (J=6.0 Hz), 8H, OCH_2.	92.8	93.67	8.82 Hz
(6)	$[L]_2Sb[S_2P(OC_4H_9)_2]$	6.90-7.90, m, 20H, Ph, 11.6, s, 2H, OH; 0.98,d, (J= 1 Hz),12H, CH_3, 1.98, m, 2H, CH, 4.00,d, (J=6.0 Hz), 4H, OCH_2	91.4	92.16	8.72 Hz
(7)	$[L']Sb[S_2P(OC_2H_5)_2]$	6.95-7.90, m, 10H, Ph, 1.45, t, (J=7.1 Hz), 12H, CH_3, 4.65, q, (J=3.5 Hz), 8H, OCH_2	92.3	–	–
(8)	$[L']Sb[S_2P(OC_3H_7)_2]$	6.95-8.00, m, 10H, Ph, 1.70, d, (J=7.1 Hz), 12H, CH_3; 4.80, m, 2H, OCH	90.4	–	–
(9)	$[L']Sb[S_2P(OC_4H_9)_2]$	6.95-7.85, m, 10H, Ph, 0.90, d, (J=7.1 Hz),12H, CH_3, 1.85, m, 2H, CH, 4.05, d, (J=6.0 Hz), 4H, OCH_2	90.6	91.75	8.92 Hz

Table IV. ^{13}C NMR Spectral Data of Some Mixed-Ligand Complexes of Antimony(III) (δ ppm)

Compound No	Compound	$-C_6H_4$[a]	C=N	OCH_2	OCH	CH	CH_3
(2)	$[L]_2Sb[S_2P(OC_2H_4)_2]$	135.8, 130.4, 129.6 140.4, 130.0, 130.8	158.4	48.46			18.32
(3)	$[L]Sb[S_2P(OC_3H_7)_2]_2$	134.6, 130.6, 128.4 139.8, 129.9, 130.4	158.8		68.45		18.90
(5)	$[L]Sb[S_2P(OC_4H_9)_2]_2$	132.6, 130.6, 129.9 138.8, 128.5, 130.6	160.6	47.28		30.42	19.92
(8)	$[L']Sb[S_2P(OC_3H_7)_2]$	133.8, 130.3, 128.2 139.6, 129.6, 129.9	157.6		66.72		16.45
(9)	$[L']Sb[S_2P(OC_4H_9)_2]$	133.0, 130.3, 128.6 138.4, 128.6, 131.4	158.9	48.36		29.29	20.32

[a] Values are in the order of C-1, C-2, C-3, C-4, C-5, C-6

isobutyl protons appear as a doublet at δ 0.96 ppm due to CH_3 protons,a multiplet centered at δ 1.90 ppm due to CH protons and a doublet at δ 3.95 ppm due to OCH_2 protons.

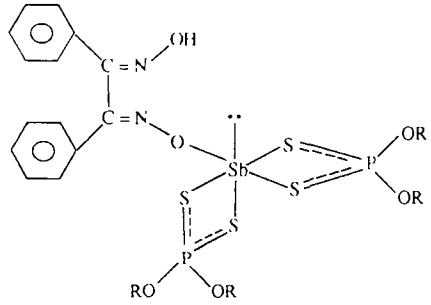
^{13}C NMR spectra of some representative compounds have been recorded (Table IV). The peak assignments are made on the basis of comparison with the reference compounds. The resonances at 130.5, 129.0, 132.8 and 139.0 ppm have been assigned, respectively, to the C-2 and C-6, C-3 and C-5 and C-1 and C-4 carbons of the phenyl group. These bands are present in the spectra of the mixed ligand complexes at almost the same position. The signal at 160 5 ppm is due to the imino carbon, which does not show any shift in the corresponding Sb(III) complexes, indicating non-involvement of the imino group in complexation.

Proton-coupled and decoupled ^{31}P NMR spectra of these complexes were obtained (Table III). In the proton decoupled spectra only one peak for each compound in the range of 90.1-92.8 ppm (J = 8.80 Hz) is observed. The ^{31}P chemical shift values observed in the parent dialkyl dithiophosphoric acids are shifted downfield in the corresponding antimony(III) complexes by 10-15 ppm. This indicates the bidentate behaviour of the dialkyl dithiophosphate moiety[15,16] in all of these derivatives which is further supported by the IR spectral data.

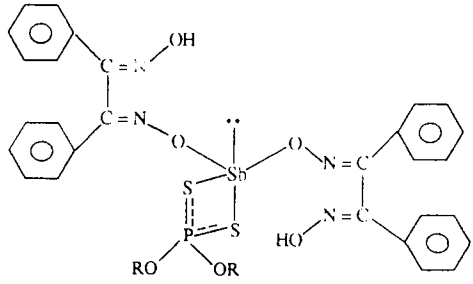
The above observations based on the physical and the spectral data show the bidentate nature of the dithiophosphate moiety and the benzildioximate moiety exhibits both unidentate and bidentate behaviour. The complexes derived from chlorobis and monochloro(benzildioximato)antimony(III) may be postulated to show trigonal bipyramidal geometry (Fig 1, b and c), while the complexes obtained from dichloro(benzildioximato)antimony(III) show a distorted octahedral geometry (Fig.1, a) if the presence of a stereochemically active lone pair is also considered in the coordination sphere.

EXPERIMENTAL

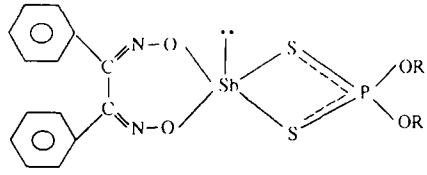
All experiments were carried out in a moisture-free atmosphere. Solvents were dried by standard methods[17]. Antimony trichloride was distilled under reduced pressure before use. Benzildioxime[18] and dialkyl dithiophosphoric acids[19-21] and their ammonium[20] salts were prepared by previously reported methods. Sulphur was determined gravimetrically as barium sulphate, nitrogen was determined by Kjeldahl's method[22] and antimony was determined iodometrically[23] after converting Sb(III) to Sb(V) by heating with $KMnO_4$, excess $KMnO_4$ was decolourised by H_2O_2 and excess H_2O_2 was removed by evaporation. 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 internal standard and ^{13}C NMR on JEOL FX-90 spectrometer using TMS as external standard and ^{31}P NMR spectra were recorded on a JEOL FX-90 spectrometer operating at 36.29 MHz using 85% H_3PO_4 as external standard. All spectra were recorded from National Chemical Laboratory, Pune. Molecular weights measured on Knauer vapour pressure osmometer in dilute



(a) Compounds (1), (3), (5)



(b) Compounds (2), (4), (6)



(c) Compounds (7), (8), (9)

Fig. 1. Suggested Structures of the Compounds

(20 g L^{-1}) chloroform solution at room temperature show the monomeric nature of the complexes.

Synthesis of Mixed-Ligand Complexes of Antimony(III)

The mixed ligand complexes of antimony(III) have been synthesized by the reaction of chloroderivatives of benzildioximatoantimony(III) with ammonium dialkyl dithiophosphates in different stoichiometric ratios.

Reaction Between Chlorobis (Benzildioximato)antimony(III) and Ammonium Salt of Diethyl Dithiophosphate in 1:1 Molar Ratio. Chlorobis(benzildioximato)antimony-(III) (1.60 g, 3.15 mmole), and ammonium diethyl dithiophosphate (0.51 g, 3.15 mmole) were mixed in 60 mL dry benzene in 1:1 molar ratio and stirred with slight heating (45-50° C) in an oil bath for about 3-4 hours. The precipitated ammonium chloride was removed by filtration, followed by removal of the solvent under reduced pressure giving the desired product, yield 1.42 g. The yellow solids were further purified by crystallization from 1:1 benzene-petroleum ether (40°-60°) mixture.

All the other derivatives of dichlorobenzildioximatoantimony(III) and monochloro-(benzildioximato)antimony(III) with the ammonium salts of dialkyl dithiophosphoric acids were synthesized similarly. The physical and analytical data is given in the Table I.

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