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Synthesis and Characterization of Mixed Phosphazene–Glycolate Complexes of Antimony(III)

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Antimony(III)triazadiphosphorine complexes, $[N(PPh_2NR')_2SbOGO]$ (where R' = -Ph or $-SiMe_3$ and G = $-CHMeCH_2-$, $-CHMeCH_2CMe_2-$, $-CH_2CH_2CH_2-$, $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$ or $-CMe_2CMe_2-$), have been synthesized by the reaction of bis-phenylated acyclic phosphazene ligand, $H[N(PPh_2NPh)_2]$, or bis-silylated acyclic phosphazene ligand, $H[N(PPh_2NSiMe_3)_2]$, with various cycloalkylenedioxyalkoxystibine, [OGOSb(OR)], (where R = -Et or $-Pr^i$) under anhydrous and inert conditions. The mixed phosphazene-glycolate derivatives of antimony(III) have been characterized by elemental analysis (C, H, N and Sb), molecular weight determination, mass, IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopies. The studies suggested a bidentate mode of bonding by phosphazene ligand that may lead to Ψ-trigonal bipyramidal coordination around the antimony. A hydrolytically stable and rubber like material has been obtained on pyrolysis of $[N(PPh_2NPh)_2SbOCH_2CMe_2CH_2O]$ which, probably, has an oligomeric composition like $\{N(PPh_2)_2(NPh)_2Sb\}_n$.

Key words: heterometallocyclophosphazenes, cycloalkylenedioxyalkoxystibine, phosphazene–glycolates, triazadiphosphorines, cyclometallaphosphazenes

In the last four decades, a substantial amount of work has been done on reactions of cyclotriazaphosphazene with various nucleophiles and electrophiles. The literature survey revealed that mainly substitution reactions to the out side of P—N ring system of cyclotriazaphosphazene (2,2,4,4,6,6-hexachloro-1,3,5-2λ^5,4λ^5,6λ^5-triazaphosphorines) [1–6] were considered. Phosphazene moiety has been treated as one of the potential precursor for producing inorganic polymers, ceramics and materials for "high-tech" purposes. They have also found applications in producing non-burning textile fibers, advanced elastomers [7–10], rechargeable lithium battery [12–13], beside their multidimensional use as biomedical materials [14–15]. In the recent past, cyclometallophosphazenes, having transition or non transition metals as building blocks in the P—N ring skeleton, have been reported, which have created lot of interest in the *academia* [16–18], due to their versatile structural aspects as well as physical properties. This is evident from the literature that the derivatives containing Sb—O and Sb—S linkages are well known [19–22], however, there are scanty information available on Sb—N linkages particularly with cyclophosphazene ring system [1,2,16,17]. In continuation of our earlier work [23–27], the synthesis and

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characterization of antimony(III)phosphazene-glycolate complexes of the type $[N(PPh_2NSiMe_3)_2SbOGO]$ and $[N(PPh_2NPh)_2SbOGO]$ is reported herein. The cycloalkylenedioxyalkoxystibines are used as starting material, knowing that these glycolates have already been utilized as antioxidants and catalysts in the manufacture of artificial fibers [28]. The development of a polymer has been tried from these heterometallocyclophosphazenes and the polymerization of compound **4**, $[N(PPh_2NPh)_2SbOCH_2CMe_2CH_2O]$, has resulted in a rubber like material.

EXPERIMENTAL

All experimental manipulations were carried out under dry nitrogen atmosphere with rigorous exclusion of moisture by using standard Schlenk techniques, since the reactants as well as the products appear to be susceptible to the moisture. The solvents (toluene, benzene, ethanol, isopropanol and methylene chloride) were dried by a standard method prior to use and kept under nitrogen atmosphere. The bis-phenylated phosphazene ligand, $H[N(PPh_2NPh)_2]$, bis-silylated phosphazene ligand, $H[N(PPh_2NSiMe_3)_2]$ and cycloalkylenedioxyalkoxystibines were synthesized by using literature method [28–30]. The glycols were procured commercially and distilled prior to use. Elemental analysis, particularly C, H and N, was done in the microanalytical laboratory, R.R.L., Jammu and antimony was estimated by iodometric titration [31]. Molecular weights were determined by cryoscopy in freezing benzene.

IR spectra were recorded in KBr mulls on Perkin Elmer-377 spectrophotometer in the range 4000–400 cm^{-1}. ^1H, ^{13}C NMR spectra were recorded on Jeol FX 90 Q MHz using TMS as external reference and ^{31}P NMR spectra were done on Bruker DRX 300(120MHz) using 85% H_3PO_4 as external reference. The mass spectrophotometric analysis (EI) was carried out on ESQUIRE–3000 (BRUKER-DALTONICS).

Synthesis of the complexes

(i) Reaction of cyclopropylenedioxyisopropoxystibine, $[OCH(CH_3)CH_2OSb(OPr^i)]$, with bis-phenylated phosphazene ligand, $H[N(PPh_2NPh)_2]$, in 1:1 molar ratio

A methylene chloride solution (about 30 ml) of 1.55 g (2.73 mmol) of phenylated phosphazene ligand, $H[N(PPh_2NPh)_2]$, was added slowly through dropping funnel to a methylene chloride solution (about 30 ml) of 0.70 g (2.73 mmol) of antimony(III)glycolates, $[OCH(CH_3)CH_2OSb(OPr^i)]$. The contents were stirred for ~2 hours and during this time a very slight change in the color was observed. Now, the reaction mixture was refluxed for ~3 hours, which resulted a dark orange color of the content. The liberated isopropanol and an excess of solvent was removed under reduced pressure. The compound was dried finally *in vacuo* for 3 hours that yielded the product in 97% yield as dark orange semi-solid.

The similar procedure and stoichiometry was followed for the synthesis of the complexes **1–5** except slight difference in refluxing period. These compounds were also obtained quantitatively as dark orange semi-solids.

(ii) Reaction of cyclopropylenedioxyethoxystibine, $[OCH(CH_3)CH_2OSb(OEt)]$, with bis-silylated phosphazene ligand, $H[N(PPh_2NSiMe_3)_2]$, in 1:1 molar ratio

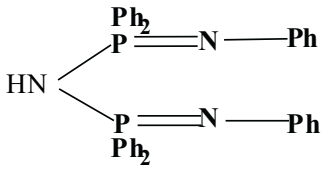
About 30 ml of toluene solution of 0.78 g (1.39 mmol) of bis-silylated phosphazene ligand, $[HN(PPh_2NSiMe_3)_2]$ was added dropwise to the toluene solution (about 30 ml) of 0.33 g (1.39 mmol) of antimony(III)glycolate, $[OCH(CH_3)CH_2OSb(OEt)]$, with constant stirring at room temperature. The contents were kept stirring for 1–2 hours in the same condition, albeit no reaction appear to occur. Now, the contents were refluxed for about 3 hours on a reaction column. The color of reaction mixture changed to yellow orange from colorless in ~45 minutes. The liberated ethanol was distilled azeotropically and an excess of solvent was removed under reduced pressure that resulted the complex in 92% yield as yellow semi solid.

Analyses confirmed the compositions indicated.

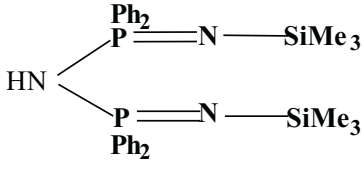
The complexes **6–10** were synthesized following the same procedure and stoichiometry. These compounds were obtained in about 92% yield as yellow/light yellow semi-solids. Though, all the complexes (**1–10**) were sufficiently spectroscopically pure, however, they could be further purified by washing with dried carbon tetrachloride.

RESULTS AND DISCUSSION

The following two acyclic bis-phenylated (**A**) and bis-silylated phosphazene (**B**) ligands have been used during the present course of investigations:



(**A**)



(**B**)

The acyclic phenylated phosphazene ligand (**A**) was reacted with various glycolates of antimony(III)isopropoxide in 1:1 molar ratio in methylene chloride under an inert and anhydrous conditions that resulted the compounds **1–5** correspond to formula $[N(PPh_2NPh)_2SbOGO]$ (Scheme 1).

Scheme 1

$$H[N(PPh_2NR')_2] + OGOSb(OR) \xrightarrow[\text{Reflux}]{C_6H_5CH_3 \text{ or } CH_2Cl_2} [N(PPh_2NR')_2SbOGO] + ROH$$

[where R' = -Ph (**1–5**) or $-SiMe_3$ (**6–10**), R = -Et or Pr^i, G = $-CHMeCH_2-$ (**1**), $-CHMeCH_2CMe_2-$ (**2**), $-CMe_2CMe_2-$ (**3**), $-CH_2CMe_2CH_2-$ (**4**), $-CH_2CH_2CH_2-$ (**5**), $-CHMeCH_2-$ (**6**), $-CHMeCH_2CMe_2-$ (**7**), $-CMe_2CMe_2-$ (**8**), $-CH_2CMe_2CH_2-$ (**9**) or $-CH_2CEt_2CH_2-$ (**10**)]

Similarly, the compounds of the type $[N(PPh_2NSiMe_3)_2SbOGO]$ have been obtained in quantitative yield, when acyclic bis-silylated phosphazene ligand, $H[N(PPh_2NSiMe_3)_2]$, was reacted with various glycolates of antimony(III)ethoxide in equimolar ratio in refluxing toluene under an inert atmosphere. These reactions appeared to be sluggish at room temperature, but become faster on refluxing. The alkoxy, (-OEt or $-OPr^i$) group attached to antimony were eliminated as EtOH or Pr^iOH and this replacement induced the cyclization of phosphazene moieties. The liberated ethanol was removed azeotropically, while isopropanol was evaporated along with the solvent *in vacuo*. The compounds with ligand (**A**) were obtained as orange semi solid and those of ligand (**B**) as yellow orange semi solid. All these compounds are soluble in common organic solvents, but insoluble in CCl_4 and found to be susceptible to the moisture even in traces.

The micro elemental analyses, particularly C, H, N and Sb, of all the complexes was found reliable to the molecular formula of the complexes. The molecular weight determination (cryoscopically) of the represented compounds indicated the monomeric nature of these complexes in freezing benzene. The mass spectrophotometric analyses (EI) of few complexes have revealed the presence of molar ion (M^+) peak. The compounds **4** and **7** have shown molar ion peak at m/z 789 (5%) and 795 (18%), respectively. In addition to the molar peak, the rest of fragmentation pattern in these compounds was in accordance to the pattern observed for the parent ligand. The base peak for **4** was found at m/z 506 (100%), which corresponds to $[(Ph_2P)_2NSb]$ ion while in compound **7**, the base peak was found at m/z 607 (100%), which corresponded to $[N(PPh_2N)_2SbSiMe_3]$ ion.

IR spectra of these complexes have shown the characteristic absorptions for νP—N bands in the region 1275–1120 cm^{-1}, which are in accordance with the symmetric nature of νP—N—P system. The disappearance of a strong band for νNH at 3345 cm^{-1} and appearance of new bands for νSb—N in the region 520–480 cm^{-1} has been observed, which is suggestive of νSb—N bond formation [24,29]. The band for νC—O (glycolate moiety) was found with a slight shift towards the NIR in the range 1040–920 cm^{-1} and the band for νSb—O occurs in the region 700–690 cm^{-1}. Relevant IR data are given in Table 1.

Table 1. IR spectral data of compounds $[N(PPh_2NPh)_2SbOGO]$ and $[N(PPh_2NSiMe_3)_2SbOGO]$ (in cm^{-1}).

Compd. No.	νP=N	νP–N–P (Ring vibrations)	νC–O	νSb–O	νSb–N
1	1600,vs	1260–1120	1030,s	690,s	520,m
2	1600,vs	1270–1120	1030,m	690,s	520,m
3	1590,vs	1260–1120	1030,m	690,s	510,m
4	1590,vs	1260–1120	1020,m	690,s	520,m
5	1590,vs	1260–1120	1030,m	680,s	500,m
6	1600,vs	1270–1120	1030,m	690,s	520,m
7	1600,vs	1260–1120	1020,m	690,s	510,m
8	1600,vs	1270–1120	1030,m	690,s	510,w
9	1610,vs	1275–1120	1040,m	700,s	520,w
10	1590,vs	1260–1130	920,m	690,s	480,m

s = strong, vs = very strong, m = medium and w = weak

The ^{1}H NMR chemical shift (in $CDCl_3$) of these complexes shows the absence of the signal for -NH proton (δ 4.5–5.0 ppm) [29] and also for protons of alkoxy group, which indicates the complexation between antimony(III)glycolate and phosphazene ligand. The phenyl protons, -PPh_2 and -NPh, in the complexes with ligand (**A**) were found as two multiplets in the region δ 6.35–7.90 ppm, while the protons for -PPh_2 in the complexes with ligand (**B**) were also found as multiplet in the region δ 6.76–8.04 ppm. The chemical shifts for -$SiMe_3$ and various protons of glycolate moiety have been observed in their characteristic region, but with a slight chemical shift towards the upfield. In ^{31}P NMR, one singlet was found in each complex of ligand (**A**) and (**B**), but with a down field shift (compare to the parent ligands) in the range δ 11–12 ppm and δ 5–9 ppm, respectively. The ^{31}P chemical shift for the complexes with ligand (**A**)

and (**B**) was observed in the region δ 18–19 ppm and δ 15–20 ppm as singlet, respectively. The occurrence of a singlet in these complexes is due to the equivalence of phosphorus nuclei in the molecule, which suggests the symmetric nature of species. The ^{13}C NMR spectra of these compounds do not show any appreciable change, compared to parent reactants. However, the disappearance of chemical shift for the ethyl and isopropyl carbons supported the formation of the complexes. The ^{1}H, ^{13}C and ^{31}P NMR data of these complexes are summarized in Table 2.

Table 2. NMR spectral data of compounds [$N(PPh_2NPh)_2SbOGO$] and [$N(PPh_2NSiMe_3)_2SbOGO$].

Compd. No	^{1}H Chemical Shift (δ ppm)	^{31}P Chemical Shift (δ ppm)	^{13}C Chemical Shift (δ ppm)
1	1.15-1.25,d,3H(-CH_3) 2.90-3.10,d,2H(-OCH_2) 3.30-3.85,m,1H(-OCH) 6.35-7.10,m,20H(-PPh_2) 7.25-7.95,m,10H(-NPh)	19.16,s	20.50,s(-CH_3) 46.80,s(-OCH_2) 120-127,m(-NPh) 128-134,m(-PPh_2)
2	1.00-1.60,m,9H(-Me) 2.90-3.10,d,2H(-OCH_2) 3.90-4.20,t,1H(-OCH) 6.50-7.90,m,30H(-Ph)	19.20,s	23.15,s(-Me_2) 28.10,d(-CH_3) 33.85,s(-CH_2) 44.80,d(-OCH_2) 119-127,m(-NPh) 128-134,m(-PPh_2)
3	1.24,s,12H(Me_2) 6.55-7.85,m,30H(-Ph)	19.10,s	25.50,s(-Me_2) 79.58,d(-CH) 120-127,m(-NPh) 128-134,m(-PPh_2)
4	0.80,s,6H(-CH_3) 3.30,s,4H(-OCH_2) 6.50-7.90,m,30H(-Ph)	19.05,s	21.09,s(-Me_2) 45.40,s(-OCH_2) 69.04,s(-C-) 118-127,m(-NPh) 128-135,m(-PPh_2)
5	3.10-3.60,t,2H(-CH_2) 3.55-3.65,t,4H(-OCH_2) 6.55-7.90,m,30H(-Ph)	18.24,s	33.90,s(-CH_2) 59.46,s(-OCH_2) 121-127,m(-NPh) 128-133,m(-PPh_2)
6	0.12,s,18H(-$SiMe_3$) 0.90-1.16,d,3H(-Me) 3.16-3.60,m,2H(-OCH_2) 3.70-3.90,q,1H(-OCH) 6.96-8.04,m,20H(-Ph)	17.43,s	8.48,s(-$SiMe_3$) 33.90,s(-OCH) 60.80,s(-OCH_2) 127-138,m(-PPh_2)
7	0.12,s,18H(-$SiMe_3$) 3.12-3.50,m,2H(-OCH_2) 3.60-3.80,m,1H(-OCH) 7.12-8.08,m,20H(-Ph)	20.14,s	8.42,s(-$SiMe_3$) 23.25,s(-Me_2) 28.02,d(-CH_3) 34.90,s(-CH_2) 44.86,d(-OCH) 127-138,m(-PPh_2)
8	0.12,s,18H(-$SiMe_3$) 1.24,s,12H(Me_2) 6.96-8.04,m,20H(-Ph)	15.43,s	8.45,s(-$SiMe_3$) 24.55,s(-Me_2) 78.60,d(-OC) 125-138,m(-PPh_2)

Table 2 (continuation)

9	0.12,s,18H(-$SiMe_3$) 0.90,s,6H(-Me) 7.00-8.10,m,20H(-Ph)	20.85,s	8.45,s(-$SiMe_3$) 22.09,s(-Me_2) 45.90,s(-OCH_2) 69.00,s(-C-) 126-139,m(-PPh_2)
10	0.12,s,18H(-$SiMe_3$) 0.60-0.96,t,6H(-CH_3) 1.10-1.28,q,4H(-CH_2) 3.48,s,4H(-OCH_2) 6.76-8.00,m,20H(-Ph)	17.17,s	8.40,s(-$SiMe_3$) 25.85,s(Me) 35.60,s(-CH_2) 61.90,s(-OCH_2) 127-138,m(-PPh_2)

*NMR in $CDCl_3$; s = singlet, d = doublet , t = triplet, q = quartet and m = multiplet

Structural features: Our efforts to get a single crystal for X-ray analyses were unsuccessful. Therefore, it would not be possible to predict the precise structure for these complexes. However, the micro elemental analysis, molecular weight determination and mass spectral studies have supported the formation of these complexes and monomeric nature as well. The IR and ^{1}H NMR have shown the disappearance of -NH proton, while ^{13}C NMR data indicated the elimination of ethoxy and isopropoxy group. Occurrence of a singlet with downfield shift in ^{31}P NMR has favored the symmetric nature of complexes and equivalence of phosphorus nuclei in the molecule. Further, on the basis of literature [22,27], a Ψ-trigonal bipyramidal (Ψ = lone pair of electron at equatorial position) coordination around the antimony may plausibly be proposed for these complexes, where ligand behaved in a bidentate manner.

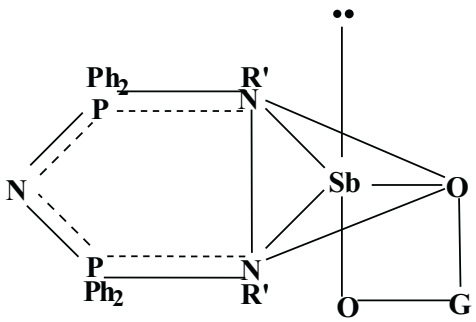


Figure 1. Ψ-Trigonal bipyramidal geometry of the complexes [$N(PPh_2NR')_2SbOGO$]; (where Ψ = lone pair of electrons and R' = -Ph (**1–5**) or -$SiMe_3$ (**6–10**) and G = -$CHMeCH_2$-, (**1**), (**6**); -$CHMeCH_2CMe_2$-, (**2**), (**7**); -CMe_2CMe_2-, (**3**), (**8**); -$CH_2CMe_2CH_2$-, (**4**), (**9**); -$CH_2CH_2CH_2$-, (**5**) or -$CH_2CEt_2CH_2$- (**10**)).

Pyrolysis: The compound (**4**), [$N(PPh_2NPh)_2SbOCH_2CMe_2CH_2O$], produces a rubber like material, when pyrolysed at 160–180°C in pyrex glass for 2 hours.

$$[N(PPh_2NPh)_2SbOCH_2CMe_2CH_2O] \xrightarrow[2\text{ hours}]{160–180°C} [N(PPh_2)_2(NPh)_2Sb]_n$$

This light yellow colored material was soluble in common organic solvents but insoluble in water. It is a hydrolytically stable material, as it remains unchanged for a long time when kept in open. Mass spectrum of this compound has given a molar peak m/z 688 (73.4%) and base peak at m/z 77 (100%). The m/z 688 may be assigned to the monomeric unit of the polymeric material. The molecular weight of this material (cryoscopically) was found 3246, which indicates an oligomeric formation rather than a polymeric system. Perhaps, this material may have the composition $[N(PPh_2)_2(NPh)_2Sb]_n$ (M.W. 688.06), since no chemical shifts were observed for the protons of glycolate moiety (present in the parent compound) in ^1H NMR spectrum.

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