Synthesis and IR Study of some Tin(IV) Hypophosphito Adducts and Compounds

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Abstract

New tin(IV) hypophosphito derivatives and adducts were synthesized; discrete and infinite chain structures are suggested on the basis of infrared spectra, $H_2PO_2^-$ acting as a bridged bidentate; $H_2PO_2^-$ turns into HPO_3^{2-} while reacting with $SnBu_3Cl$.

Introduction

Single crystal X-ray diffraction studies on $Cu[(C_2H_5)_2PO_2]_2$ [1], $Cu[(nC_4H_9)_2PO_2]_2$ [2], $Cu[(C_6H_{13})_2PO_2]_2$ [3] and $Mn[(CH_3)_2PO_2]_2$ [4] have been reported. Their structure consists of infinite chains of copper and manganese atoms linked by double phosphinate bridges. From these X-ray results indicating the strong coordinating power of $R_2PO_2^-$, it appeared interesting to study the interactions of $H_2PO_2^-$ with some tin(IV) halides and organometallic compounds to obtain new hypophosphito adducts and compounds, the structure of which will be proposed on the basis of IR spectra.

Experimental

$TMNH_2PO_2H_2O$ (L) (TMN = tetramethylammonium)

L was obtained by mixing stoichiometric amounts of H_2PO_2H and TMNOH (10% in water). The solution was stirred and water removed under vacuum at 50 °C. The white powder obtained was recrystallized from absolute ethanol.

Anal. Calc. C, 30.57; H, 10.19; N, 8.92. Found: C, 30.88; H, 10.31; N, 8.92%.

$SnX_4H_2PO_2TMN\frac{1}{6}EtOH$

When stoichiometric amounts (ratio 1:1) of SnX_4 in benzene and L in absolute ethanol were mixed, precipitation occurred. After at least 1 h stirring, white and yellow precipitates (X = Cl and Br respectively) were collected and dried *in vacuo*.

Anal. Calc. for X = Cl: C, 12.92; H, 3.72; N, 3.47; Cl, 34.87. Found: C, 12.55; H, 3.71; N, 3.44; Cl, 35.04%.

Calc. for X = Br: C, 8.88; H, 2.56; N, 2.39; Br, 54.64. Found: C, 8.52; H, 2.43; N, 2.32; Br, 54.56%.

$(SnPh_3Cl)_2L$ (A); $SnBu_2HPO_3$ (B), $SnMe_2(H_2PO_2)_2$ (C); $SnPh_2(H_2PO_2)_2H_2O$ (D); $SnBu_2(H_2PO_2)_2$-$\frac{1}{6}EtOH$ (E)

On mixing ethanolic solutions of $SnPh_3Cl$ and $SnBu_3Cl$ respectively with ethanolic solutions of L in the ratio 2:1, A and B precipitate; C, D, E precipitate when ethanolic solutions of L are added respectively to ethanolic solutions of $SnMe_2Cl_2$, $SnPh_2Cl_2$ and $SnBu_2Cl_2$ in the ratio 1:1. The precipitates (all of them are white) were collected after at least 1 h stirring and dried *in vacuo*.

Anal. Calc. for A: C, 52.75; H, 4.83; N, 1.54; Cl, 7.80. Found: C, 52.47; H, 4.96; N, 1.53; Cl, 7.40%.

Calc. for B: C, 30.70; H, 6.08. Found: C, 30.70; H, 6.28%.

Calc. for C: C, 8.61; H, 3.59. Found: C, 8.67; H, 3.55%.

Calc. for D: C, 34.23; H, 3.80. Found: C, 34.46; H, 3.70%.

Calc. for E: C, 26.99; H, 6.21. Found: C, 27.15; H, 5.97%.

The infrared spectra were scanned on a P.E.580 infrared spectrophotometer as Nujol mulls using CsI plates. The elemental analyses were performed by the analytical laboratory of the Department of Chemistry, University of Padova, Italy or the Service Central d'Analyses, Vernaison, France.

Results and Discussion

Our assignments of the vibrations of the ligand in the titled adducts and compounds confirm those of Abenoza and Tabacik on alkaline hypophosphites [5].

$SnX_4H_2PO_2TMN\frac{1}{6}EtOH$ (X = Cl, Br)

The strong and sharp band at 300 cm^{-1} when X = Cl shifting to 210 cm^{-1} when X = Br is the band of Eu symmetry characteristic of νSnX_4; it indicates

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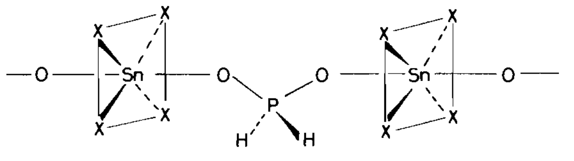

Fig. 1. Suggested structure of $SnBr_4H_2PO_2TMN\frac{1}{6}EtOH$: an infinite chain with bridged $H_2PO_2^-$.

D_{4h} symmetry [6–8]. νSnO, obscured by the strong $SnCl_4$ band mentioned above, is localized at 280 cm^{-1} in the IR spectrum of $SnBr_4H_2PO_2TMN\frac{1}{6}EtOH$. The suggested structure is an infinite chain with bridged $H_2PO_2^-$ (Fig. 1).

$(SnPh_3Cl)_2H_2PO_2TMN$

The strong band at 338 cm^{-1} on the IR spectrum of $SnPh_3Cl$, absent on the IR spectrum of $SnPh_3Cl_2$-TMN, indicates D_{3h} symmetry for the SnC_3 group. The absence of this band indicates a flat SnC_3 group in this adduct as in $SnPh_3NO_3$ pyridine N-oxide [9]. The suggested structure is discrete with bidentate $H_2PO_2^-$ linked to two $SnPh_3Cl$ molecules (Fig. 2). νSnO is localized at 225 cm^{-1}.

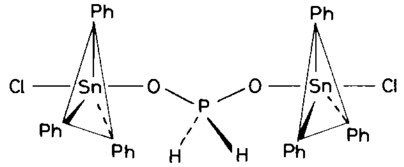

Fig. 2. Suggested structure of $(SnPh_3Cl)_2H_2PO_2TMN$ with bidentate $H_2PO_2^-$ linked to two $SnPh_3Cl$ molecules.

$R_2Sn(H_2PO_2)_2$ (R = Me, Ph, Bu)

In the methyl derivative, the absence of ν_sSnC_2, appearing at 515 cm^{-1} in $SnMe_2(SeO_4)_{1.5}TMN$ [10], reveals a linear SnC_2 group. The structure proposed is an infinite chain of tin atoms linked by double bridged bidentate $H_2PO_2^-$, the environment of the tin atom being octahedral and the methyl groups occupying *trans* positions (νSnO = 250 cm^{-1}). The structure of the phenyl derivative, because of the presence of only one band due to $\nu_{as}SnC_2$ at 300 cm^{-1}, is identical to the one of the methyl derivative (νSnO = 240 cm^{-1}). In the butyl derivative the presence of ν_sSnC_2 at 530 cm^{-1} reveals a bent SnC_2 group allowing two structures to be suggested:

(i) a discrete one with monodentate $H_2PO_2^-$, the tin atom having a tetrahedral environment

(ii) an infinite chain structure as in the methyl derivative, the length effect of the butyl groups preventing the SnC_2 group being linear; this length effect has already been reported in the IR study of $SnBu_2SeO_4$ [10] (νSnO = 270 cm^{-1}). Because of the tendency of $H_2PO_2^-$ to act as bidentate, the infinite type structure can be retained.

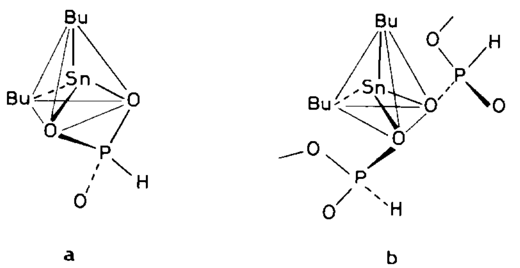

Fig. 3. Suggested structures of $SnBu_2HPO_3$: (a) discrete structure with chelating phosphite, (b) infinite chain with bridged bidentate phosphite.

$SnBu_2HPO_3$

The disappearance of ρPH_2 appearing at 810 cm^{-1} in the IR spectra of hypophosphito compounds confirms the oxidation of $H_2PO_2^-$ to HPO_3^{2-}. SnC_2 being bent (ν_sSnC_2 is localized at 532 cm^{-1}), the environment of the tin atom is tetrahedral so two structures are possible.

(i) a discrete one with chelating phosphite (Fig. 3(a))

(ii) an infinite chain with bridged bidentate phosphite (Fig. 3(b))

Conclusions

In this work, some new tin(IV) hypophosphito compounds and adducts have been synthesized. In all these compounds and adducts $H_2PO_2^-$ as $R_2PO_2^-$ mentioned above acts as a bridged bidentate. In the presence of $SnBu_3Cl$, $H_2PO_2^-$ turns into HPO_3^{2-}, this oxidation being accompanied by a Sn–C bond cleavage.

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References

1 K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, *60* (1982) 2017.
2 R. Cini, P. Colamarino, P. L. Orioli, L. S. Smith, P. R. Newman, H. D. Gillman and P. Nannelli, *Inorg. Chem.*, *16* (1977) 3223.
3 J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, *62* (1984) 891.
4 W. V. Cicha, J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson and J. Trotter, *Can. J. Chem.*, *63* (1985) 1055.
5 M. Abenoza and V. Tabacik, *J. Mol. Struct.*, *26* (1975) 95.

6 I. R. Beattie, R. Hulme and L. Rule, *J. Chem. Soc.*, (1965) 1581.

7 I. R. Beattie, R. Milne, W. Webster, H. E. Blayden, P. J. Jones, R. C. G. Killean and J. L. Lawrence, *J. Chem. Soc. A*, (1969) 482.

8 A. Saxena, J. P. Tandon and A. J. Crowe, *Inorg. Chim. Acta, 84* (1984) 195.

9 C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Organomet. Chem., 124* (1977) 151.

10 O. Sarr, *Thesis*, University of Dakar, 1988.