Synthesis and Characterization of Salicylate Derivatives of Dibutyl Sn(IV)-Ti(IV)- μ -Oxoisopropoxide

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Abstract: New Salicylate derivatives of organoheterobimetallic- μ -oxoisopropoxide $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$ have been synthesized by the thermal condensation of μ -oxoisopropoxide compound with different salicylates in different molar ratios (1:1-1:4) yielded the compounds of the type $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_{6-n}(\text{RSal})_n]$ (where n is 1-4 and RSal = Salicylate anion) respectively. The μ -oxoisopropoxide derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C , ^{119}Sn NMR).

Keywords: Metal alkoxide, Tin, Titanium, Salicylate.

Introduction

The chemistry of metal alkoxides and their applications to biology and materials science¹⁻³ are very attractive and fast growing research areas. Among the many aspects being studied, the preparation of heteronuclear molecules potential single-source precursors of high technology mixed-metal oxides is one of the most challenging.

This synthetic contribution to the field has been the combination of first-row transition metal, titanium(IV) and tin to provide precursor for mixed metal oxides. To achieve the goal its salicylate derivatives were synthesized because of their less tendency to undergo hydrolysis and prevent the phase secreation problem in forming the multicomponent oxides. In the context of the search for environment-respectful, lead- and bismuth-free chemical compounds for devices such as actuators, SnTiO_3 (ST) is investigated from first principles within DFT. The equation of state describes the equilibrium volume of SnTiO_3 is smaller than ferroelectric PbTiO_3 (PT) in agreement with a smaller Sn^{2+} radius. While ionic displacements exhibit similar trends between ST and PT, a larger tetragonality (c/a ratio) for ST results in a larger polarization. Within ST analyzes of site projected density of states and chemical bonding indicate a reinforcement of the bond covalence with respect to Pb homologue. Both PT and ST exhibit anomalous large effective charges and the dielectric constant of ST is calculated larger than PT⁴.

Volatile organometallic alkoxides are among the best precursors for the synthesis mixed metal oxides because they can be used in metal-organic-chemical-vapor-deposition (MOCVD), in sol-gel synthesis or in solid synthesis.⁵ Homogeneously dispersed bimetallic oxides in nanocrystalline or amorphous forms, of the type MA_2O_4 (where M = Mg, Ca, Mn, Co, Fe, and Zn) were prepared from bimetallic oxo-bridged alkoxides $[(RO)_2Al-O-M-O-Al(OR)_2]$, where the Al-O-M-O-Al bonds were not hydrolytically cleaved. This approach yields hydroxides $[(HO)_2Al-O-M-O-Al(OH)_2]$ which, upon thermal dehydration, yield oxides $[OAl-O-M-O-AlO]$, such that M is homogeneously dispersed with an empirical formula of MA_2O_4 . Comparative studies of the hydrolysis of alkoxo-bridged alkoxides with respect to oxo-bridged alkoxides yielded mixed metal oxide phases with lower surface areas. Recently, synthesis of homogeneously dispersed bimetallic oxides in nano crystalline or amorphous form has been reported by Klabunde *et al.*⁶ Apart from their role as precursors for mixed metal oxides the bimetallic- μ -oxoalkoxides of transition metals have been found to rank among the best catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes, and epoxides⁷⁻⁸. Molybdenum and tungsten alkoxides in their middle oxidation state have been used as a model for reductive cleavage of carbon monoxide to carbides and oxides via the Fisher-Tropsch reaction⁹. Owing to the ever-growing importance of hetero metallic alkoxides and oxoalkoxides it was considered worthwhile to synthesize the salicylate derivatives of $[Bu_2SnO_2Ti_2(OPr^i)_6]$.

Experimental

All manipulations have been carried out under anhydrous conditions and the solvents and reagents used were purified and dried by standard methods¹⁰. The general technique and physical measurement were carried out as described elsewhere¹¹⁻¹³. $[Bu_2SnO_2Ti_2(OPr^i)_6]$ was prepared in laboratory by reported method¹⁴. The isopropoxy groups in the μ -oxoisopropoxide compound and liberated isopropanol formed in preparation of Salicylate derivatives were estimated oxidimetrically¹⁵. Tin and titanium were estimated gravimetrically¹³. The derivatives of $[Bu_2SnO_2Ti_2(OPr^i)_6]$ were decomposed in conc. HCl and extracted in dil. HCl, tin was precipitated as sulphide (pH 5-6), filtered and estimated as SnO_2 ¹³. The H_2S was boiled off completely from the filtrate and titanium was estimated as TiO_2 via the formation of titanium-phenazone complex¹³.

The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of $4000-400\text{ cm}^{-1}$. The 1H , ^{13}C , and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer.

Synthesis of Derivatives of Dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with Salicylate

Reaction of $[Bu_2SnO_2Ti_2(OPr^i)_6]$ with Methyl Salicylate (HMeSal) in 1:1 Molar Ratio

The compound $[Bu_2SnO_2Ti_2(OPr^i)_6]$ (2.074g, 2.91 mmol) and methyl salicylate (0.442 g, 2.91 mmol) were refluxed in (~50) ml benzene for 3 hrs at $\sim 100^\circ C$ in a flask connected to short distillation column. The liberated isopropanol was collected continuously at $72-78^\circ C$ as a binary azeotrope of isopropanol-benzene¹⁶. The isopropanol in azeotrope was estimated oxidimetrically to check the completion of the reaction. The excess of the solvent was then removed under reduced pressure ($45^\circ C/1\text{mm}$) yielding a yellowish red highly viscous product.

Similar procedure was adopted for the preparation of other derivatives of $[Bu_2SnO_2Ti_2(OPr^i)_6]$ with salicylates *i.e.* methyl salicylate (HMeSal), ethyl salicylate (HEtSal), and

phenyl salicylate (HPhSal) in stiochiometric ratio of 1:1, 1:2, 1:3, and 1:4 molar ratios. The details are given in (Table 1) along with analytical data.

Table 1. Analytical data.

S.No.	Compound g, mmol	Ligand g, mmol	Molar Ratio	Refluxing time (Hrs)	Product	Anal found (calcd)		
						Pr ⁱ OH, g	Sn, %	Ti, %
1.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 2.074(2.91)	HMeSal 0.442(2.91)	1:1	3	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (MeSal)]	0.16 (0.17)	14.4 (14.7)	11.4 (11.6)
2.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 1.201(1.68)	HMeSal 0.512(3.37)	1:2	6 ¹ / ₂	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (MeSal) ₂]	0.18 (0.20)	13.6 (13.2)	10.3 (10.4)
3.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.713(1.00)	HMeSal 0.457(3.00)	1:3	8	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (MeSal) ₃]	0.18 (0.18)	12.2 (12.0)	9.6 (9.5)
4.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.561(0.79)	HMeSal 0.479(3.15)	1:4	14	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (MeSal) ₄]	0.20 (0.19)	10.9 (11.0)	8.5 (8.6)
5.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 1.269(1.78)	HEtSal 0.295(1.78)	1:1	3	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (EtSal)]	0.10 (0.11)	14.7 (14.5)	11.4 (11.4)
6.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.991(1.39)	HEtSal 0.459(2.78)	1:2	7	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (EtSal) ₂]	0.16 (0.17)	12.5 (12.8)	9.9 (10.1)
7.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.976(1.37)	HEtSal 0.677(4.10)	1:3	10	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (EtSal) ₃]	0.23 (0.25)	11.6 (11.5)	8.9 (9.1)
8.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.590(0.83)	HEtSal 0.546(3.31)	1:4	14	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (EtSal) ₄]	0.21 (0.20)	10.3 (10.5)	8.1 (8.2)
9.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 1.404(1.97)	HPhSal 0.424(1.97)	1:1	3 ¹ / ₂	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (PhSal)]	0.12 (0.12)	13.4 (13.7)	10.5 (10.8)
10.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.837(1.17)	HPhSal 0.506(2.35)	1:2	7	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (PhSal) ₂]	0.14 (0.14)	11.6 (11.6)	8.8 (9.1)
11.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.786(1.10)	HPhSal 0.713(3.31)	1:3	9 ¹ / ₂	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (PhSal) ₃]	0.22 (0.20)	10.2 (10.1)	7.6 (7.9)
12.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.545(0.76)	HPhSal 0.658(3.06)	1:4	14	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (PhSal) ₄]	0.18 (0.18)	9.0 (8.9)	7.2 (7.0)

HMeSal = Methyl salicylate; HEtSal = Ethyl salicylate; HPhSal = Phenyl salicylate.

Results and Discussion

A number of reactions of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with bidentate salicylates *i.e.* methyl salicylate (HMeSal), ethyl salicylate (HEtSal), and phenyl salicylate (HPhSal) are performed in different molar ratios in refluxing benzene results in to the formation of the products of type $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{RSal})]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{RSal})_2]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{RSal})_3]$, and $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{RSal})_4]$ ($R = \text{Me, Et, Ph}$). The general reaction can be given as follows.

where $n = 1-4$ and HRSal = alkyl/aryl salicylate. The isopropanol liberated during the course of reaction is collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction and it has been observed that only four out of six of isopropoxy groups of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide could be replaced with salicylates. Further replacement of fifth and sixth isopropoxy groups could not be achieved even with an excess of ligand (salicylate) and prolonged refluxing time (approx. 20 hours).

All the salicylate derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide are found to be yellowish product from gel type to solid product, soluble in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly.

Infrared Spectral Studies

The IR spectra of salicylates show a broad band in the region $3000-2700\text{ cm}^{-1}$ due to $\nu(\text{O-H})$, the absence of this band in the derivatives of μ -oxocompounds indicates the deprotonation of these ligands. The band appearing at $\sim 1650\text{ cm}^{-1}$ in salicylates due to $\nu(\text{C-O})$ shows a downward shift of $15-25\text{ cm}^{-1}$ in the derivatives, indicating the coordination of the carbonyl oxygen of the salicylate to the metal atom. A strong band observed at $\sim 1245\text{ cm}^{-1}$ in salicylates due to phenolic $\nu(\text{C-O})$ vibrations is shifted $10-20\text{ cm}^{-1}$ higher in the derivatives indicating bond formation of phenolic oxygen of salicylate to the metal atom. The spectra of the 1:1 to 1:3 salicylate derivatives of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$ show absorption bands in the region $1360-1340\text{ cm}^{-1}$ and $1165-1150\text{ cm}^{-1}$ are the characteristics of *gem*-dimethyl portion and combination band $\nu(\text{C-O}+\text{OPr}^i)$ of the terminal and bridging isopropoxy group respectively.¹⁷⁻¹⁸ No peak is observed at 1165 cm^{-1} in the spectrum of 1:4 salicylate derivatives indicates the absence of terminal isopropoxy group. A band appeared at approximately 950 cm^{-1} is due to $\nu(\text{C-O})$ stretching of bridging isopropoxy group. However, all these bands are also observed in 1:5 and 1:6 salicylate derivatives as that found in 1:4 salicylate derivatives of μ -oxoisopropoxide compound reveals the presence of bridging isopropoxy group even in the 1:6 salicylate derivatives.

A number of bands appearing in the region $700-400\text{ cm}^{-1}$ are due to M-O stretching vibrations in these derivatives¹⁹. The bands related to phenyl groups in the salicylate derivatives are observed at their usual positions in the IR spectra as observed in the ligands²⁰. The IR spectra of the derivatives indicate that salicylates behave as monobasic bidentate ligands.

NMR Spectral Studies

¹H NMR

The ¹H NMR spectra of salicylates show a broad singlet at $\sim \delta 12.8\text{ ppm}$ due to phenolic O-H proton, the absence this peak in the derivatives confirms their deprotonation. The peak at $\sim \delta 3.8\text{ ppm}$ due to methyl protons of methyl salicylate and methene proton of the ethyl salicylate is found to overlap with the multiplet centered at $\delta 4.1\text{ ppm}$ due to methine protons of the isopropoxy group in the derivatives of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$.

¹H NMR spectra of all the Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide show broad multiplet centered between $\delta 0.8-1.2\text{ ppm}$ due to the

intermixing of methyl protons of isopropoxy groups along with butyl groups on tin. The signals due to phenyl ring protons of salicylate moiety are observed at their usual positions ($\delta 6.4 - 87.6$ ppm) in all the derivatives.

^{13}C NMR (Proton Decoupled)

The ^{13}C NMR spectra of 1:1 to 1:3 Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide compound shows two prominent peaks at $\delta \sim 27.4$ and $\delta \sim 27.9$ ppm assignable to the methyl carbon of terminal and intermolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group is confirmed by the two signals observed at $\delta \sim 62.6$ ppm and $\delta \sim 62.8$ ppm. The other peaks are found at 25.44, 25.27, 24.1, and 13.43 due to C-1, C-2, C-3, and C-4 of the butyl group. Further the 1:4 schiff base derivatives of μ -oxoisopropoxide show the absence of terminal isopropoxy group. These signals are also observed in 1:5 and 1:6 schiff base derivatives of μ -oxo compound not the removal of the bridging isopropoxy group. The peaks observed in the region $\delta 124-138$ ppm are due to carbon atoms on benzene ring; however, the peak observed at about $\delta 168$ ppm is due to ring carbon linked to the ester group and a peak observed at about $\delta 187$ ppm is due to carbon of the ester group ($-\text{COOR}$)²¹.

^{119}Sn NMR

A sharp signal around at $\delta -192.4$ ppm in the ^{119}Sn NMR spectrum of derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide is attributed to the hexacoordination about Sn atom in the all compound²².

The aforesaid spectral study and elemental analysis suggest the tentative structures of the Salicylate derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide of the type $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{RSal})]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{RSal})_2]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{RSal})_3]$, and $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{RSal})_4]$.

Conclusion

On the basis of above analytical studies the following tentative structure have been assigned to the salicylate derivatives of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$ [Figure 1 (a)&(b)].

Figure 1. [(a) & (b)].

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References

1. (a) Hubert-Pfalzgraf L G, *Inorg Chem Commun.*, 2003, **6**, 102; (b) Seisenbaeva G A, Gohil S and Kessler V G, *Inorg Chem Commun.*, 2004, **7**, 18; (c) Veith M, Mathur S and Mathur C, *Polyhedron*, 1998, **17**, 689.
2. (a) Nassif N, Roux C, Coradin T, Rager M N, Bouvet O M M and Livage J, *J Mater Chem.*, 2003, **13**, 203; (b) Alfaya A A S and Kubota L T, *Quim Nova.*, 2002, **25**, 835; (c) Coiffier A, Coradin T, Roux C, Bouvet O M M and Livage J, *J Mater Chem.*, 2001, **11**, 2039.
3. (a) Veith M, *J Chem Soc Dalton Trans.*, 2002, **12**, 2405 (b) Kessler V G, *Chem Commun.*, 2003, **11**, 1213; (c) Yu Z Q, Wang C X, Li C, Gu X T and Zhang N, *J Cryst Growth.*, 2003, **256**, 210.
4. Matar S F, Baraille I and Subramanian M A, *Chem Phys.*, 2009, **355**, 43.
5. Hench L L and West J K, *The sol-gel process Chem Rev.*, 1990, **90**, 33.
6. Stark J V, Park D G, Lagadic I, and Klabunde K J, *J Chem Mater.*, 1996, **9**, 1904.
7. Klabunde K J, Stark J V, Koper O, Mohs C, Park D G, Decker S, Jiang Y, Lagadic I and Zhang D, *J Phys Chem.*, 1996, **100**, 12142.
8. Koper O, Lagadic I and Klabunde K J, *Chem Mater.*, 1997, **9**, 838.
9. Chisholm M H, *J Organomet Chem.*, 1987, **344**, 77.
10. Perrin D D, Armarego W L F and Perrin D R, *Purification of Laboratory Chemicals*, 2nd Edn (Pergamon Press, New York), 1980.
11. Sharma H K, and Kapoor P N, *Polyhedron*, 1988, **7**, 1389.
12. Ramchandran R, Singh B, Narula A K, Gupta P K and Kapoor R N, *Polyhedron*, 1985, **4**, 1007.
13. Vogel A I, *A Text Book of Quantitative Analysis*, Longman, London, 1989.
14. Sharma H K and Kumar Rajesh; *Indian J Chem.*, 2008 **47A**, 854.
15. Bradley D C, Halim F M A and Wardlaw W, *J Chem Soc.*, **3450** (1950).
16. Sharma Malti, Bhagi A. K., Sharma H. K., Priti, Kansal Ritu, Kumar Ram and Kapoor P N, *Indian J Chem.*, 2005, **44A**, 1.
17. Lynch C T, Masdiyanni K S, Smith J S and Grawford W J, *Anal Chem.*, 1964, **36**, 2332.
18. Koznov V A, Kuzlova N I, Turova N Ya and Nekrasov Yu S, *Zh Neorg Khim.*, 1979, **24**, 1526.
19. Nakamoto K, McCarthy P J, Ruby A and Martel A E, *J Am Chem Soc.*, 1961, **83**, 1066.
20. Sonika, Narula A K, Vermani O P, Sharma H K, *J Organomet Chem.*, 1994, **470**, 67.
21. Shiner V J, Whittaker Jr D and Fernandes V F, *J Am Chem Soc.*, 1963, **85**, 2318.
22. Nguyen T T, Ogwuru N and Eng G, *Appl Organomet Chem.*, 2000, **14**, 345.