

From the data available<sup>5,6</sup> in respect of nioxime and salicylaloxime it can be concluded that the chelates derived from the alicyclic ligand are less stable than those from the aromatic one. In other words, removal of conjugation in the ring system of the reagent results in decrease of thermal stability of its metal chelates. Similar observations were made by Bottei *et al.*<sup>7</sup> in their studies on 8-hydroxy-1,2,3,4-tetrahydroquinoline. Salicylaloxime, resacetophenoneoxime and 2-hydroxy-1-naphthaldoxime form six-membered chelate rings with the metal bonded to phenolic oxygen and nitrogen of the oxime group. All the three oximes form 1:2 complexes (metal to ligand ratio) with the three metals. 2-Hydroxy-1-naphthaldoxime chelates are thermally more stable than the corresponding salicylaloxime chelates. The enhanced thermal stability can be accounted for by the presence of an additional aromatic ring<sup>8</sup> and consequent higher electron density at the reactive centre. The higher thermal stability of resacetophenoneoxime complexes was ascribed to the higher electron density at the reactive centre<sup>9</sup>.

The authors are thankful to the CSIR, New Delhi, for the award of a junior research fellowship to one of them (R.S.N.).

#### References

- MICHIO MASHIMA, *J. chem. Soc. Japan*, **74** (1953), 622.
- GUSEV, S. I., KUMOV, V. I. & SOKOLOVA, E. V., *Zh. analit. Khim.*, **15** (1960), 180.
- SESHADRI NAIDU, R. & RAGHAVA NAIDU, R., *Indian J. Chem.*, **15A** (1976), 69.
- VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1961, 480, 497, 512.
- LIPTAY, G., PAPP MOLNAR, E. & BURGER, K., *J. inorg. nucl. Chem.*, **34** (1969), 247.
- DUVAL, C., *Inorganic thermogravimetric analysis* (Elsevier, London), 1953, 236, 259, 347.
- BOTTEI, R. S. & O'REILLY, J. C., *J. inorg. nucl. Chem.*, **30** (1968), 1481.
- BOTTEI, R. S. & MCEACHERN, C. P., *J. inorg. nucl. Chem.*, **32** (1970), 2653.
- SESHAGIRI, V. & BRAHMAJI RAO, S., *Z. analyt. Chem.*, **262** (1972), 275.

### Complexes of Triphenylarsine Oxide with Trichlorotin(IV) & Trichlorotitanium(IV) Alkoxides & Dichlorotitanium(IV) Dialkoxides

R. C. PAUL, PRATIBHA SHARMA, HARINDER SINGH,  
P. K. GUPTA & S. L. CHADHA

Department of Chemistry, Panjab University  
Chandigarh 160014

Received 19 July 1976; accepted 9 February 1977

**Complexes of SnCl<sub>3</sub>(OR), TiCl<sub>3</sub>(OR) and TiCl<sub>2</sub>(OR)<sub>2</sub> (where R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>2</sub>H<sub>4</sub>Cl and C<sub>2</sub>H<sub>2</sub>F<sub>3</sub>) with triphenylarsine oxide having 1:1 stoichiometry have been prepared and characterized on the basis of analytical and IR data.**

**T**HE preparation and properties of the complexes of triphenylarsine oxide with various metal halides have been well studied. However, very little work has been reported on the complexes of metal alkoxides with donors<sup>1</sup> and of these there is none

with triphenylarsine oxide. We report here the reactions of triphenylarsine oxide with the compounds SnCl<sub>3</sub>(OR), TiCl<sub>3</sub>(OR) and TiCl<sub>2</sub>(OR)<sub>2</sub>. The products formed have been characterized on the basis of IR spectra.

All manipulations and reactions were carried out in anhydrous conditions. Tin(IV) chloride and titanium(IV) chloride were distilled prior to use. The alcohols were dehydrated and distilled before use. Compounds of the type TiCl<sub>3</sub>(OR) were prepared by literature methods<sup>2-4</sup> and their purity was ascertained on the basis of analytical and m.p. data. The compounds TiCl<sub>2</sub>(OR)<sub>2</sub><sup>5,6</sup> and SnCl<sub>3</sub>(OR).ROH<sup>7</sup> were also prepared by literature methods.

The complexes with triphenylarsine oxide were prepared by mixing its solution in chloroform or dry ethanol with the benzene or ethanolic solution of TiCl<sub>3</sub>(OR), TiCl<sub>2</sub>(OR)<sub>2</sub> or SnCl<sub>3</sub>(OR).ROH. A solid product was obtained by keeping for overnight. The complexes were filtered under anhydrous conditions, washed with benzene/ethanol and dried *in vacuo*.

Titanium<sup>8</sup> and chlorine<sup>9</sup> were estimated gravimetrically as titanium dioxide and silver chloride respectively.

Analyses of the complexes (Table 1) suggest 1:1 stoichiometry [alkoxide : (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO] for all of them. Limited solubility of these complexes in solvents such as benzene, chloroform and nitrobenzene precludes the cryoscopic determination of their molecular weights and conductance measurements. Lowering of  $\nu$ As=O of the pure ligand (880 cm<sup>-1</sup>) to the region 825-855 cm<sup>-1</sup> in the spectra of the complexes indicates the coordination of its oxygen to tin or titanium. The shifted  $\nu$ As=O in these complexes is quite close to the value reported for the SnCl<sub>4</sub>.2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO complex<sup>10</sup>. The  $\nu$ C—O mode arising from the C—O—M (M = Ti or Sn) moiety of the alkoxide part in these complexes is either present at the same position as in the case of pure alkoxide or is slightly shifted towards higher wave numbers and this is in accord with the presence of

TABLE 1 — MELTING POINT AND ANALYTICAL DATA OF THE COMPLEXES\* OF SnCl<sub>3</sub>(OR), TiCl<sub>3</sub>(OR) and TiCl<sub>2</sub>(OR)<sub>2</sub> WITH TRIPHENYLARSINE OXIDE (L)

Complex	m.p. (°C)	Found (calc.), %	
		Metal	Cl
TiCl <sub>3</sub> (OCH <sub>3</sub> ).L	297-98	9.43 (9.44)	20.62 (20.99)
TiCl <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> ).L†	295-96	8.84 (9.18)	21.20 (20.42)
TiCl <sub>3</sub> (OC <sub>2</sub> H <sub>4</sub> Cl).L†	297-99	8.38 (8.61)	26.04 (25.56)
TiCl <sub>3</sub> (OC <sub>2</sub> H <sub>2</sub> F <sub>3</sub> ).L	288-89	9.71 (8.32)	17.79 (18.50)
TiCl <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> .L	294-95	9.89 (9.52)	14.78 (14.12)
TiCl <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> .L	290-91	9.56 (9.19)	21.37 (20.42)
TiCl <sub>2</sub> (OC <sub>2</sub> H <sub>4</sub> Cl) <sub>2</sub> .L	285-86	7.60 (7.98)	24.25 (23.67)
TiCl <sub>2</sub> (OC <sub>2</sub> H <sub>2</sub> F <sub>3</sub> ) <sub>2</sub> .L	298-300	7.65 (7.49)	11.02 (11.11)
SnCl <sub>3</sub> (OCH <sub>3</sub> ).L	170	20.38 (20.52)	18.30 (18.41)
SnCl <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> ).L	195	20.20 (20.03)	17.80 (17.97)
SnCl <sub>3</sub> (OC <sub>2</sub> H <sub>7</sub> ).L	160	19.85 (19.57)	17.70 (17.97)
SnCl <sub>3</sub> (OC <sub>2</sub> H <sub>4</sub> Cl).L	209-11	19.84 (18.93)	22.04 (22.64)
SnCl <sub>3</sub> (OC <sub>2</sub> H <sub>2</sub> F <sub>3</sub> ).L	204-6	18.52 (18.36)	16.17 (16.47)

\*Titanium complexes are yellow solids, while the tin complexes are white solids.

†Satisfactory carbon and hydrogen analyses were also obtained for these complexes.

coordinated alkoxy group<sup>11</sup> in these complexes. The  $\nu_{\text{Ti-O}}$  vibration is present around 600-630  $\text{cm}^{-1}$  in these complexes.

The empirical formula for the complexes  $\text{SnCl}_3(\text{OR}) \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  suggests the possibility of five-coordinated tin. Infrared spectra of these complexes show a broad band of strong intensity in the region 510-525  $\text{cm}^{-1}$ . This band may tentatively be assigned



to the Sn—Sn vibration and such an assignment compares well with a similar band present in the region 480-530  $\text{cm}^{-1}$  in the spectra of  $\text{SnCl}_3(\text{OR}) \cdot \text{ROH}$ <sup>12</sup> and  $\text{Sn}(\text{OR})_2(\text{acac})_2$ <sup>13</sup>. Thus the present 1:1 complexes appear to have alkoxy bridged dimeric structures. The 1:2 adducts with pyridine<sup>14</sup> or 8-hydroxyquinoline<sup>15</sup> do not have such a band which supports the above view.  $\nu_{\text{Sn-Cl}}$  vibration appears in the region 310-320  $\text{cm}^{-1}$  and this value is close to those reported for hexacoordinated tin<sup>16</sup> (cf.  $\text{SnCl}_6^{2-}$  absorbs at 312  $\text{cm}^{-1}$ ).

The complexes  $\text{TiCl}_3(\text{OR}) \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  and  $\text{TiCl}_2(\text{OR})_2 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  may be five-coordinated monomers but this does not agree with their insolubility in common organic solvents. Alternatively the present complexes may have six-coordinated structure acquired either by alkoxy bridging or chlorine bridging. The IR spectra in the region 600-250  $\text{cm}^{-1}$  is very complex and precludes ascertaining of any of the above possibilities. The  $\nu_{\text{Ti-Cl}}$  vibration in these complexes appears in the region 300-370  $\text{cm}^{-1}$  and this is the region where  $\nu_{\text{Ti-Cl}}$  of six-coordinated titanium also absorbs<sup>17</sup>.

Thanks are due to the Head of the Chemistry Department, Banaras Hindu University, Varanasi, for the far IR spectra.

#### References

- BRADLEY, D. C., *Progress in inorganic chemistry*, Vol. 2 (Interscience, London), 1960, 303.
- YASTREBOV, V. V. & CHERNYSHEV, A. V., *Zhur. obshch. Khim.*, **40** (1970), 604.
- CLARK, R. J. H., *The chemistry of titanium and vanadium* (Elsevier, London), 1968, 301.
- PAUL, R. C., SHARMA, P., GUPTA, P. K. & CHADHA, S. L., *Inorg. chim. Acta*, **20** (1) (1976), 7.
- JENNINGS, J. S., WARDLAW, W. & WAY, W. J. R., *J. chem. Soc.*, (1936), 637.
- PAUL, R. C., GUPTA, P. K., GULATI, M. & CHADHA, S. L., *J. less-common Metals* (communicated).
- BRADLEY, D. C., CALDWELL, E. V. & WARDLAW, W., *J. chem. Soc.*, (1957), 3039.
- BRADLEY, D. C., HANCOCK, D. C. & WARDLAW, W., *J. chem. Soc.*, (1952), 2773.
- VOGEL, A. I., *A text book of inorganic quantitative analysis* (Longmans, Green, London), 1961, 461.
- PHILLIPS, D. J. & TYREE, S. Y., *J. Am. chem. Soc.*, **83** (1961), 1806; CLARK, J. P., LANGFORD, V. M. & WILKINS, C. J., *J. chem. Soc.*, A (1967), 792; KUMAR DAS, V. G. & KITCHING, W., *J. organometal. Chem.*, **13** (1968), 523.
- PAUL, R. C., MADAN, H. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **36** (1974), 737; **37** (1975), 447.
- PAUL, R. C., SINGH, P., MAKHNI, H. S. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **32** (1970), 2141.
- KAWASKI, Y., TANAKA, T. & OKAWARA, R., *J. organometal. Chem.*, **6** (1966), 95.
- PAUL, R. C., SINGH, H. & CHADHA, S. L., *Indian J. Chem.*, **15A** (1977), 121.
- PAUL, R. C. & CHADHA, S. L., unpublished work.
- BEATTIE, I. R., MCQUILLON, G. P., RULE, L. & WEBSTER, M., *J. chem. Soc.*, (1963), 1514.
- CLARK, R. J. H. & ERRINGTON, W., *J. chem. Soc.*, A (1967), 258.

## Complexes of Dibutyltin(IV) with 2-Aminobenzoic Acids & 2-(Monotertiary-arsino)benzoic Acids

S. S. SANDHU, J. K. SINDHU & G. K. SANDHU

Department of Chemistry, Guru Nanak Dev University Amritsar

Received 2 February 1976; revised 21 July 1976  
accepted 3 February 1977

Complexes of di(*n*-butyl)tin(IV) have been prepared with (a) 2-aminobenzoic acid, (b) *N*-methyl-2-aminobenzoic acid, (c) 2-amino-5-chlorobenzoic acid, (d) *N*-phenyl-2-aminobenzoic acid, (e) 2-(diphenylarsino)benzoic acid and (f) 2-{di(*p*-tolyl)arsino}benzoic acid. On the basis of analytical data these complexes have been assigned three types of formulae, (i)  $(\text{C}_4\text{H}_9)_2\text{SnL}_2$ , (ii)  $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{L}'_2)\text{L}'\text{H}$  and (iii)  $(\text{C}_4\text{H}_9)_2(\text{L}'')\text{Sn}_2\text{O}$ , where LH is (a), (c), (d), (f), L'H is (b) and L''H is (e). Complexes of the type (i) and (iii) are monomeric. The infrared data indicate the absence of bonding between nitrogen or arsenic of these ligands and tin(IV). However, bidentate nature of carboxylate group of these ligands has been established on the basis of IR spectra. Hexa-coordinated structures have been suggested for all the complexes except  $\{(\text{C}_4\text{H}_9)_2(\text{L}'')\text{Sn}_2\text{O}$  which is penta-coordinated.

PREPARATION and characterization of complexes of 2-amino-, *N*-methyl-2-amino-, 2-amino-5-chloro-, *N*-phenyl-2-amino-, 2-(diphenylarsino)- and 2-{di(*p*-tolyl)arsino}-benzoic acids with dibutyltin(IV) oxide are reported in this paper. A penta-coordinated tin(IV) complex with 2-aminobenzoic acid has been reported<sup>1</sup>.

2-Amino-, *N*-methyl-2-amino-, *N*-phenyl-2-aminobenzoic acids were available commercially and used after purification. 2-Amino-5-chlorobenzoic acid<sup>2</sup>, 2-(diphenylarsino)benzoic acid and 2-{di(*p*-tolyl)arsino}benzoic acid<sup>3</sup> were prepared by known methods. Esters of aminobenzoic and substituted aminobenzoic acids were prepared as described earlier<sup>4</sup>. Di(*n*-butyl)tin(IV) oxide was procured from M/s Alfa Inorganics.

The complexes were prepared by refluxing an equimolar mixture of the ligand (0.1 mole) and dibutyltin oxide (0.1 mole) in a 1:1 mixture of dry benzene and absolute ethyl alcohol (30 ml) for 4 hr. Dean and Stark separator was used to remove water from the reaction mixture. After removing the solvent the solid product was crystallized from dry pet. ether (60-80°) and dried *in vacuo*.

Elemental analysis was obtained from Australian Microanalytical Service. Tin was estimated as tin dioxide. Molecular weights were determined in benzene by cryoscopic method. The IR spectra were recorded in nujol in the range 4000-650  $\text{cm}^{-1}$  on a Carl Zeiss Specord 71 instrument. NMR spectra were recorded on Tesla BS 487 NMR spectrometer (80 MHz).

Analytical results (Table 1) indicate three types of stoichiometries: (i)  $(\text{C}_4\text{H}_9)_2\text{SnL}_2$ , (ii)  $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{L}'_2)(\text{L}'\text{H})$  and (iii)  $\{(\text{C}_4\text{H}_9)_2(\text{L}'')\text{Sn}_2\text{O}$  (where LH is 2-aminobenzoic acid, 2-amino-5-chlorobenzoic acid,