

Coordination Compounds of Di-*n*-butyltin Ethylene Glycolate, Di-*n*-butyltin Succinate & Di-*n*-butyltin *o*-Phthalate with Some Nitrogen & Oxygen Donors

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Di-*n*-butyltin ethylene glycolate (DBTEG), di-*n*-butyltin succinate (DBTS) and di-*n*-butyltin *o*-phthalate (DBTP) react with donors (L) such as dimethyl sulphoxide, pyridine N-oxide, pyridine and γ -picoline to give the adducts of compositions DBTEG. 2L, DBTS. L and DBTP. L respectively. The structure of these adducts has been elucidated with the help of elemental analyses, infrared and Mössbauer spectroscopy.

A large number of alkyltin alkoxides are known to undergo electrophilic reactions¹ but their stable coordination adducts have not been reported so far. Di-*n*-butyltin ethylene glycolate (DBTEG) has been assigned an uncommon ten-membered ring structure²⁻⁴. However, the chemistry of this compound remains largely unexplored. Further, not much work is reported on the coordination properties of the carboxylates⁵. Therefore, electron acceptor potentials of di-*n*-butyltin succinate (DBTS), di-*n*-butyltin *o*-phthalate (DBTP) and DBTEG towards dimethyl sulphoxide (DMSO), pyridine N-oxide (py N \rightarrow O), pyridine (py) and γ -picoline (γ -pic) have been investigated and the results are presented in this paper.

The solvents used were dried by the conventional methods. Di-*n*-butyltin oxide (Akzo Chemical Ltd, Kirby), ethylene glycol, *o*-phthalic acid, succinic acid, dimethyl sulphoxide, pyridine, pyridine-N-oxide and γ -picoline (all BDH, pure) were used as such. Di-*n*-butyltin ethylene glycolate, di-*n*-butyl *o*-phthalate and di-*n*-butyl succinate were prepared by the known methods^{6,7}.

Infrared spectra were recorded in nujol or KBr on Perkin-Elmer spectrophotometers, models 337 and 621. Mössbauer spectra were recorded at 77 K using Harwell Mössbauer spectrometer equipped with a 256 multichannel analyser in the transmission geometry and the velocity drive in constant acceleration mode. The source used was Ba^{119m}SnO₃. The spectra were analysed to Lorentzian lines through the least square fitting.

Reactions of di-*n*-butyltin ethylene glycolate, *o*-phthalate and succinate with dimethyl sulphoxide, pyridine N-oxide, pyridine and γ -picoline—A mixture of DBTEG, DBTP or DBTS and DMSO, py N \rightarrow O, py or γ -pic in the molar ratio 1 : 2 (acid : base) in dry

dichloromethane or benzene was refluxed for 2-3 hr under dry N₂ atmosphere until a colourless liquid was obtained. After evaporating the solvent, a white solid was obtained in each case which was filtered, dried and analysed. Relevant physical and analytical data are recorded in Table 1.

Di-*n*-butyl ethylene glycolate complexes have the composition DBTEG. 2L while the rest have the compositions DBTS. L and DBTP. L. The compounds are solids, insoluble in common organic solvents thus precluding their molecular weight determination by cryoscopic method. Conductance measurements of the millimolar solutions of these compounds show them to be non-electrolytes.

The $\nu_{as}COO$ and ν_sCOO are observed at ~ 1580 and $1430-1410\text{ cm}^{-1}$ respectively, in DBTP and DBTS. The ν_{CO} , ν_{SnOC} , ν_{SnC_2} and ν_{OSn} modes are located at 1065 , $1030-1025$, $560-545$ and $415-265\text{ cm}^{-1}$ respectively, in DBTP, DBTS and DBTEG⁵. The characteristic modes of pyridine and γ -picoline⁸ (i.e. C=C and C=N) are known to absorb at $1580-1480\text{ cm}^{-1}$. The ν_{NO} and ν_{SO} are detected at 1265 and 1055 cm^{-1} in pure pyridine N-oxide and DMSO⁸. All these modes undergo spectral shifts in the adducts isolated. For example, $\nu_{as}COO$, are observed at $1670-1655\text{ cm}^{-1}$ with positive shift of nearly 90 cm^{-1} , while ν_sCOO appear at $1405-1370\text{ cm}^{-1}$ with negative shift of $70-90\text{ cm}^{-1}$. This observation is in accordance with those reported⁹. Whereas, in the complexes of DBTP and DBTS the ν_{CO} , ν_{SnOC} , ν_{SnC_2} and ν_{OSn} remain unaltered or undergo slight positive shifts, in DBTEG adducts, they are observed at 1050 , $1015-1010$ and $390-310\text{ cm}^{-1}$ respectively, thus showing negative spectral shifts. Pyridine and γ -picoline modes are revealed at $1660-1530\text{ cm}^{-1}$ in the complexes with upward change in frequency by $50-80\text{ cm}^{-1}$. DMSO and py N \rightarrow O adducts show ν_{NO} and ν_{SO} modes at $950-960\text{ cm}^{-1}$. The ν_{C-S} has been found to shift

Table 1—Physical and Analytical Data of Adducts of Di-*n*-butyltin Ethylene Glycolate, *o*-Phthalate and Succinate with DMSO, py N \rightarrow O, py and γ -pic

Compound	m.p. °C	Found (Calc) %		
		Sn	N	S
1. DBTEG.2DMSO	220-21	29.9(31.8)	—	8.0(8.6)
2. DBTEG.2py-N \rightarrow O	203	32.0(30.5)	3.0(3.6)	—
3. DBTEG.2py	219-22	32.0(31.8)	3.2(3.6)	—
4. DBTEG.2 γ -pic.	220-22	31.3(30.6)	2.9(3.6)	—
5. DBTP.DMSO	175(d)	25.8(24.9)	—	6.5(6.7)
6. DBTP.py-N \rightarrow O	118-20	23.7(24.0)	2.6(2.8)	—
7. DBTP.py	208-11	24.7(24.0)	2.7(2.9)	—
8. DBTP. γ -pic.	164-66	24.8(24.1)	2.8(2.6)	—
9. DBTS.DMSO	174-77	27.6(27.7)	—	7.0(7.5)
10. DBTS.py-N \rightarrow O	130-34	26.0(26.6)	3.0-(3.2)	—
11. DBTS.py	184-88	28.0(27.6)	3.1(3.3)	—
12. DBTS. γ -pic.	175-77	26.5(26.7)	3.0(3.1)	—

DBTEG, DBTP, DBTS and the adducts Nos 1,3,5,8 and 10 were also analysed for carbon and hydrogen. The data corresponded with the compositions of the compounds given.

Table 2—Mössbauer Spectral Data of a Few Compounds

Compound	δ	Δ	Γ_1	Γ_2
DBTEG	1.18	3.15	1.05	1.10
DBTEG.2DMSO	1.32	3.10	0.98	1.05
DBTP.DMSO	1.46	3.58	0.91	0.93
DBTS.rp-pic.	1.44	3.61	0.91	1.17

from 720 to 700-680 cm^{-1} ($\Delta\nu=20-40 \text{ cm}^{-1}$) in these adducts. In the above complexes with oxygen donors, a new band has been invariably observed between 410 and 380 cm^{-1} which is attributed to O \rightarrow Sn bonds⁵. A comparison of the infrared spectral data with those of the known compounds⁵ support penta-coordinated tin in all these complexes.

The Mössbauer spectra of a few of these compounds have been recorded. The adducts show only one type of quadrupole doublet (Table 2). Therefore, it is expected that tin atom has only one kind of environment in a particular compound. The δ and Δ values for all the compounds are quite close to those reported for organotin(IV) halides, their adducts and organotin carboxylates¹⁰ which have five-coordinated tin atoms. This is in accordance with the conclusions obtained from infrared spectra.

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References

- 1 Bloodworth A J & Davies A G *Organotin compounds* Vol. I, edited by A K Sawyer, (Marcel Dekker, New York), 1971 and references therein.
- 2 Mehrotra R C & Gupta V D, *J organometal Chem*, **4** (1965) 237.
- 3 Considine Wm J, *J organometal Chem*, **5** (1966) 263.
- 4 Pommier J C & Valade, J, *J organometal Chem*, **12** (1968) 433.
- 5 Poller R C, *The chemistry of organotin compounds* (Logos Press, London), 1973 and references therein.
- 6 Borstein J, Laliberte B R, Andrews T M & Montermoso J C, *J Am chem Soc.* **24** (1959) 886.
- 7 Andrews T M, Bower F A, Laliberte B R & Montermoso J C, *J Am chem Soc.* **80** (1958) 4102.
- 8 Bellamy L J, *Infrared spectra of complex molecules* (John Wiley, New York), 1966.
- 9 Lever A B P & Ogden D, *J chem Soc (A)*, (1967) 2041.
- 10 Greenwood N N & Gibbs T C, *Mössbauer spectroscopy* (Chapman and Hall, London), 1971.