Mössbauer Spectra of Hexaco-ordinate Tin Compounds Containing Tin–Sulphur Bonds

By R. C. POLLER,* J. N. R. RUDDICK, and J. A. SPILLMAN†

(*Chemistry Department, Queen Elizabeth College, Campden Hill Road, London, W.8*)

Summary Mössbauer parameters for complexes of the type SnX_4Y_2 ($X = S$, $Y = N$ or O) are reported; the quadrupole splittings for compounds with *cis*-Y groups are *ca.* 1 and those for the *trans*-compounds are *ca.* 2 mm s^{-1}.

THE significance of the presence of a quadrupole splitting and of the magnitude of the splitting in the Mössbauer spectrum of a tin compound is not always clear.[1,2] Point charge calculations[3] suggest that, for compounds of the type SnX_4Y_2, quadrupole splittings of the *trans*-isomers should be twice those for the *cis*-compounds, but these predictions have only been tested for organotin compounds. We now report Mössbauer parameters for 16 compounds, SnX_4Y_2, where $X = S$ and $Y = N$ or O (see Table).

The gross stereochemistry of compounds (**1**)—(**3**), where all the ligands are bidentate, is unambiguous. In a previous i.r. study[4] we assigned configurations to compounds (**4**)—(**7**); the trimethylamine oxide complex (**7**) was shown to be *cis* whereas the other monodentate ligands gave *trans*-adducts. Allowing for the assumptions made in the point charge approximation the results are in good agreement with prediction. The quadrupole splittings Δ(*trans*) *ca.* 2 and Δ(*cis*) *ca.* 1 mm s^{-1} are about half the values obtained for hexaco-ordinate organotin compounds R_2SnZ_4. The previous configurational assignments are confirmed and it is possible to assign configurations to the remaining compounds in the Table.

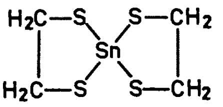
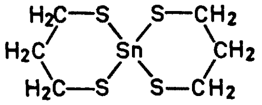
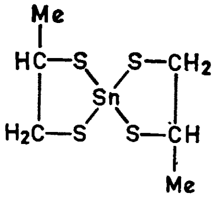
In contrast to the results now reported no quadrupole splitting was observed for the SnX_4Y_2 compounds $SnCl_4$,-2,2′-bipyridyl[5] and $SnCl_4,MeSCH_2CH_2SMe$[6] and simple

---

† Present address: Chemistry Department, Borough Polytechnic, Borough Road, London, S.E.1.

electronegativity considerations are inadequate for prediction of the occurrence of a quadrupole splitting.[1] It has been suggested that inductive effects are better guides to bond polarities but although some success has been obtained by consideration of the Taft σ^* constants of substituents attached to tin[2] these constants are not available for the more contentious cases such as hexamethylditin. However the inductive electron release for trimethyl derivatives of the Group IVB elements is known to be in the order $Me_3Si < Me_3Ge < Me_3Sn$[7] and the fact that the $+I$ effect of Me_3Si is much higher than that of Me is evident from consideration of the following apparent ionization constants ($K_b \times 10^4$) $MeNH_2$ 5·0, $Me_3SiCH_2NH_2$ 9·1, $EtNH_2$ 5·6.[8] It is clear that there is a very considerable difference between the inductive effects of the Me_3Sn and Me groups and yet $Me_3SnSnMe_3$ has no observable quadrupole splitting.[2] An entirely satisfactory method of correlating quadrupole splitting with structural parameters is therefore still awaited.

Mössbauer parameters and configurations of hexaco-ordinate tin complexes

No.	Complex	δ^a (mm s^{-1})	Δ (mm s^{-1})	Γ_1^b	Γ_2^b	Configuration
(1)	 ,2,2′-bipyridyl	1·06	1·17	0·81	0·88	*cis*
(2)	,1,10-phenanthroline^c	1·03	1·06	0·85	0·85	*cis*
(3)	,2,2′-bipyridylamine	1·09	1·26	0·83	0·87	*cis*
(4)	,(pyridine)$_2$^{c}	1·06	1·86	0·81	0·90	*trans*
(5)	,(4-methylpyridine)$_2$	0·99	1·88	0·75	0·77	*trans*
(6)	,$(Et_2SO)_2$	1·04	1·94	0·75	0·85	*trans*
(7)	,$(Me_3NO)_2$	0·62	1·15	0·77	0·89	*cis*
(8)	 ,2,2′-bipyridyl	1·07	1·02	0·83	0·83	*cis*
(9)	,1,10-phenanthroline	1·07	0·87	0·85	0·85	*cis*
(10)	,(pyridine)$_2$	1·08	1·77	0·81	0·85	*trans*
(11)	,(4-methylpyridine)$_2$	1·07	1·79	0·73	0·85	*trans*
(12)	 ,2,2′-bipyridyl	1·06	1·08	0·80	0·85	*cis*
(13)	,1,10-phenanthroline	1·08	1·17	0·78	0·85	*cis*
(14)	,$(Et_2SO)_2$	1·07	1·95	0·85	0·88	*trans*
(15)	,(4-aminopyridine)$_2$	0·99	1·38	0·84	0·90	*cis*
(16)	$(PhS)_4Sn$,2,2′-bipyridyl	1·14	0·81	0·74	0·85	*cis*

[a] Isomer shifts refer to Sn^{IV} oxide.

[b] Γ = line width at half peak-height.

[c] Previously reported[9] values: compound (2) $\delta = 0·96$, $\Delta = 1·00$; compound (4) $\delta = 1·05$; $\Delta = 1·84$ mm s^{-1} [isomer shifts converted from the Mg_2Sn into the Sn^{IV} oxide scales by addition of 1·82 (ref. 10)].

(*Received, April 20th,* 1970; *Com.* 579.)

---

[1] K. M. Ali, D. Cunningham, M. J. Frazer, J. D. Donaldson, and B. J. Senior, *J. Chem. Soc.* (*A*), 1969, 2836.
[2] R. V. Parish and R. H. Platt, *J. Chem. Soc.* (*A*), 1969, 2145.
[3] B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc.* (*A*), 1969, 143.
[4] R. C. Poller and J. A. Spillman, *J. Chem. Soc.* (*A*), 1966, 1024.
[5] N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc.* (*A*), 1967, 1679.
[6] J. Philip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, 1968, 7, 1895.
[7] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, 2, 154.
[8] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 98.
[9] L. M. Epstein and D. K. Straub, *Inorg. Chem.*, 1965, 4, 1551.
[10] R. H. Herber, Tech. Rept. Ser. No. 50, Internat. Atomic Energy Agency, Vienna, 1966, 121.