Octahedral and Tetrahedral Diorganotin Bisdithiocarbamates

By BRIAN W. FITZSIMMONS

(*Department of Chemistry, Birkbeck College, London, W.C.*1)

ON the basis of Mössbauer spectral data presented here it is proposed that diorganotin bisdithiocarbamates $R_2Sn[S_2CNR'R'']_2$ (R = Ph; R',R'' = various) are hexa-co-ordinate octahedral complexes containing *cis*-diorganotin units and S-bonded bidentate chelating dithiocarbamate-groups. Certain others of these derivatives (R = alkyl; R',R'' = various) do not appear to have this structure and a lower co-ordination state is indicated. The Mössbauer data do not of themselves allow us to positively identify this lower co-ordination state but penta- and tetra-co-ordination are obvious possibilities and we prefer the latter because such compounds would contain two unidentate dithiocarbamato-groups, and the rather more complicated situation involving one unidentate and one bidentate ligand is not favoured.

Mössbauer parameters for diorganotin bisdithiocarbamates[a]

	$R_2Sn[S_2CNR'R'']_2$[b]	δ (mm. sec.$^{-1}$)	Δ*E* (mm. sec.$^{-1}$)
1	$Ph_2Sn[S_2CNPh_2]_2$	1·19	1·69
2	$Ph_2Sn[S_2CNEt_2]_2$	1·17	1·76
3	$Ph_2Sn[S_2CN(CH_2Ph)_2]_2$	1·08	1·66
4	$Ph_2Sn[S_2CN(CH_2)_4]_2$	1·17	1·68
5	$Bu_2Sn[S_2CN(CH_2Ph)_2]_2$	1·69	3·38
6	$Bu_2Sn[S_2CN(CH_2)_4]_2$	1·53	3·06
7	$Me_2Sn[S_2CN(CH_2)_4]_2$	1·59	2·85
8	$Bu_2Sn[S_2CNPh_2]_2$	1·72	3·21
9	$Me_2Sn[S_2CNPh_2]_2$	1·54	3·20
10	$Me_2Sn[S_2CNEt_2]_2$	1·57	3·14

[a] δ and Δ*E* are accurate to at least ± 0·2 mm. sec.$^{-1}$ and δ is expressed relative to tin(IV) oxide, with β-tin at 2·70 mm. sec.$^{-1}$; [b] All compounds gave satisfactory analyses.

The Mössbauer data (Table) are interpreted as follows: the quadrupole splittings for compounds 1—4 are *ca.* 1·7 mm. sec.$^{-1}$. In previous Communications[1] we have explained why splittings of this magnitude are to be associated with *cis*-octahedral structures and we may thus assign this stereochemistry to this set of compounds. We would expect[1] analogous *trans*-complexes to have quadrupole splittings of *ca.* 3·7 mm. sec.$^{-1}$, with isomeric shifts (δ) of similar magnitude to those of the *cis*-compounds. Although compounds 5—10 do indeed exhibit splittings of this magnitude, their isomeric shifts are substantially greater than those of compounds 1—4. Replacing phenyl by alkyl is expected to increase δ but the increases observed here are sufficiently great for us to conclude that compounds 5—10 are not *trans*-octahedral. Results from ^{57}Fe Mössbauer spectroscopy indicate that this change in δ is in the correct direction for a change to lower co-ordination number.

Finally, the point-charge model is not consistent with the relative quadrupole splittings observed here and we conclude that the structural change from octahedral is associated with a substantial reduction in bond length.

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[1] B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Comm.*, **1968**, 390.