New Intercalates of Graphite: ^{119}Sn Mössbauer Spectroscopy and *X*-Ray Diffractometry of Lamellar Compounds Containing Me_3SnCl and $SnCl_4$

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Summary New second-stage and third-stage intercalates of the title compounds have been prepared and characterized.

ALTHOUGH a wide range of intercalates may be formed with graphite as host,[1] to date the intercalation of tin compounds has proven extremely difficult; the possible intercalation of $SnCl_4$ has been only briefly described.[2] Recently, however, a photochemical procedure has been developed whereby a wide variety of intercalates of graphite may be obtained at room temperature,[3,4] and we here describe two new intercalates, produced by this procedure, involving Me_3SnCl and $SnCl_4$.

Intercalation was effected by irradiating an equimolar mixture of high-purity natural graphite flakes [from Kropfmuhl (Bavaria) ground in air, without subsequent annealing, to give a particle size of *ca.* 1 μm] and the tin compound in stringently dry CCl_4 (refluxed five times and distilled over a 4 Å molecular sieve under argon until Fourier transform ^{1}H n.m.r. spectroscopy and gas chromatography indicated complete purity), at 5 °C with $\lambda > 320$ nm using a high-pressure Hg lamp, for between 3 and 40 days.

X-Ray diffractometry, as well as yielding indexable peaks corresponding to the formation of second-stage and third-stage intercalates respectively for $SnMe_3Cl$ and $SnCl_4$ as intercalants (see Table), also showed that some of the graphite had not reacted [residual graphite (002) reflections]. The peaks corresponding to so-called rhombohedral graphite (101, 102, and 006), which are prominent in the original diffractograms of the ground natural flakes, disappear after reaction, proving that intercalation had indeed taken place.[5] The *c*-axis repeat distance reflects the van der Waals radius of the intercalated molecule. Thermogravimetric analysis and chemical analyses (which show an excess of chlorine) suggest that, as in other intercalation reactions occurring within a solution phase, solvent molecules are included during intercalation.[2]

Whereas the decrease in magnitude of the isomer shift and absence of resolvable quadrupole splitting for $SnCl_4$ following intercalation points to the donation of electrons from the graphite to the guest with retention of the overall tetrahedral symmetry of the molecule, the corresponding changes with Me_3SnCl may imply a difference in geometry between the intercalated and free species. This contrasts well with the recent observation[6] that little change occurs for Me_3SnCl adsorbed on to the surface of grafoil. The ease with which the intercalated Me_3SnCl and $SnCl_4$ may be chemically modified *in situ* and the role of the solvent in such reactions is currently being investigated.

TABLE. Mössbauer and *X*-ray powder diffraction data for intercalation of $SnCl_4$ and Me_3SnCl into graphite.

(A) Mössbauer (data in mm s^{-1} at 80 K, relative to SnO_2; figures for the pure materials[a] in square brackets).

	δ	Δ	Γ
$SnCl_4$	0·39(3) [0·85]	0 [0]	1·02(7)
Me_3SnCl	1·57(2) [1·43]	3·55(2) [3·32]	0·86(2)

(B) *X*-Ray

Me_3SnCl			
$d_{obs.}$/Å	$d_{calc.}$/Å	00*l*	*I*
7·925	8·186	002	W
5·405	5·457	003	SS
4·074	4·093	004	S
3·260	3·274	005	VW
2·730	2·729	006	M
2·321	2·399	007	VW
2·085	2·047	008	W
1·807	1·819	009	M
1·483	1·478	0010	W

$\bar{d}$ = 16·38(10) Å

$SnCl_4$			
$d_{obs.}$/Å	$d_{calc.}$/Å	00*l*	*I*
6·098	6·277	003	M
4·692	4·708	004	S
3·704	3·766	005	S
—	3·139	006	—
2·697	2·690	007	VW
2·352	2·354	008	W
2·089	2·092	009	M
1·871	1·883	0010	W
1·719	1·712	0011	W
1·581	1·569	0012	W

$\bar{d}$ = 18·84(9) Å

[a] From N. N. Greenwood and T. C. Gibb, in 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

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