

Graphite Intercalation Compounds with Tin Tetrachloride

Robert Schlögl and Hanns-Peter Boehm*

Institut für Anorganische Chemie
der Universität München, Meiserstraße 1,
D-8000 München 2, Germany (Fed. Rep.)

Z. Naturforsch. **39b**, 112–114 (1984);
received August 12, 1983

Graphite Intercalation Compounds,
Hexachlorostannate, Photochemistry,
Tin Tetrachloride

Intercalation compounds of graphite with SnCl_4 have been prepared by reaction in $\text{SOCl}_2/\text{CCl}_4$ or by UV irradiation in CCl_4 or 1,2-dichloroethane. Mixtures of 1st, 2nd, and 3rd stages have been obtained. Chemical analyses and ^{119}Sn Mößbauer spectra indicate that SnCl_6^{2-} ions are intercalated. Solvent molecules are co-intercalated.

Introduction

Graphite intercalation compounds (GICs) have found great interest in the recent years as indicated by several review articles written by chemists [1, 2] as well as by physicists [3, 4]. The interspaces between the carbon layers are all or only in part expanded and filled with the intercalated material. Usually several stages of a given GIC can be obtained, 1st, 2nd, 3rd stage *etc.*; the stage number indicates the number of carbon layers separating the intercalated layers in regular stacking. First stage compounds are richest in intercalate. The carbon layers as well as the intercalated layers are charged. One may distinguish between GICs with electron donors, *e.g.* alkali or alkaline earth metals, and the much larger group of acceptor compounds, *e.g.* with fluorides or chlorides of many elements [1, 2]. The carriers in the carbon layers are highly mobile, giving rise to a high electric conductivity approaching half that of copper [3].

The chlorides of the elements of the fourth main group are conspicuously missing in the list of the chlorides which are intercalated in graphite [5]. We report here on novel intercalation reactions with tin tetrachloride. Stumpp and Klink described at a recent conference [6] that GICs are obtained by reaction of graphite with $\text{H}_2\text{SnCl}_6 \cdot 6 \text{H}_2\text{O}$.

Usually, metal chlorides are reacted with graphite in a sealed ampoule at elevated temperatures. It is necessary in most cases to add some chlorine as an oxidant which leads to the positive charge of the carbon layers. Thus the GIC $\text{C}_{27}^+(\text{Al}_3\text{Cl}_{10})^-$ is produced

with $\text{AlCl}_3 + \text{Cl}_2$. Only chlorides which are in equilibrium with free chlorine at the reaction temperature are intercalated without additional chlorine. As Boeck and Rüdorff [7] found, many metal chlorides can be intercalated from solution in thionyl chloride. This was ascribed to beginning decomposition of SOCl_2 at its reflux temperature leading to Cl_2 among other compounds. We have developed a new photochemical intercalation method [8]: a dispersion of graphite in a mixture of metal chloride and CCl_4 and/or other chlorinated hydrocarbons, *e.g.* 1,2-dichloroethane, is irradiated with UV light. Chlorine atoms and other free radicals produced by photolysis act as oxidizers in the intercalation reaction. Both, reaction in SOCl_2 and photochemical intercalation were successful with SnCl_4 .

Experimental

Natural graphites of 99.9% purity from Kropfmühl, Bavaria, were used (S 40: flakes of 0.3–0.7 mm diameter, AF: finely milled to 1–10 μm).

Graphite (50 mmol = 600 mg) was suspended – in some cases with addition of KCl – in 50 ml of a solution of SnCl_4 (10 or 4.2 mmol) in CCl_4 or in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$. The solvents had been purified and dried over zeolite 4 A in darkness. A 1:1 mixture of CH_3CN and CCl_4 containing the stoichiometric quantity of LiCl was also used. The stirred suspension was irradiated under dry N_2 for 24 h, using a 100 W high pressure Hg burner (a few hours were sufficient with a medium pressure burner). The reaction was performed in Schlenk tubes from borosilicate glass. The reaction products were filtered, and dried in vacuo (10^{-3} Pa) at room temperature. The samples were handled under dry argon or nitrogen.

Results and Discussion

Intercalation was observed under the following reaction conditions:

- (1) graphite + $\text{SnCl}_4 + \text{CCl}_4$ (or $\text{C}_2\text{H}_4\text{Cl}_2$),
UV irradiation.
- (2) graphite + $\text{SnCl}_4 + 2 \text{LiCl} + \text{CCl}_4/\text{CH}_3\text{CN}$,
UV irradiation.
- (3) graphite + $\text{SnCl}_4 + 2 \text{KCl} + \text{CCl}_4$,
UV irradiation.
- (4) graphite + $\text{SnCl}_4 + \text{SOCl}_2/\text{CCl}_4$,
heating to 40 °C.

The best pathway proved to be reaction (2). A compound with 16.6% Sn has been obtained. In reaction (4) the oxidizing species is very likely a small concentration of Cl or Cl_2 produced by thermolysis of the SOCl_2 . However, this preparation method

* Reprint requests to Prof. Dr. H.-P. Boehm.
0340–5087/84/0100–0112/\$ 01.00/0

Table I. Analyses of typical reaction products.

Preparation method	Graphite	Sn [%]	Cl [%]	ratio Cl/Sn	X-ray analysis I_c in pm and stage
1 (C ₂ H ₄ Cl ₂)	S 40	5.0	9.0	6.03	1296 ± 11 (2nd st.); 1876 ± 24 (3rd st.)
3	AF	—	—	—	938 ± 6 (1st st.); 1436 ± 29 (2nd st.)
4	AF	2.6	4.8	6.18	1132 ± 15 (1st st.); 1489 ± 25 (2nd st.)

seems less satisfactory because of possible contamination of the reaction products with other decomposition products of SOCl₂.

The reaction products were extremely air-sensitive and had to be handled accordingly. X-ray diffractograms showed sharp (001) reflexes only for samples which had been vacuum-dried. Freshly prepared material produced no or very diffuse reflexes. In all cases, mixtures of different phases were obtained. There was always unreacted graphite present, too. All samples were turbostratic, there were no (*hkl*) reflexes. Evaluation of the (001) reflexes resulted frequently in I_c values for the different phases which differed by less than 335 pm, *i.e.* the thickness of a carbon layer in graphite (see Table I). There is always co-intercalation of solvent and/or its photolysis products in photochemical intercalation. Apparently, different quantities of solvent may be co-intercalated in a given stage of the GIC, giving rise to different interlayer spacings. Different quantities and different arrangements of solvent molecules have been

observed in THF-solvated potassium graphite [9]. The spacings observed by us are larger than those reported by Stumpp and Klink for a 1st stage (953 pm) or a 3rd stage (1610 pm) of their stannic chloride GICs [6].

The ratio of Cl:Sn was found by chemical analysis to be slightly higher than 6 (Table I). There is no sense in giving the C:Sn ratio because of the presence of free graphite and co-intercalation of the solvent. Even when unequivocal statements are not possible since chlorine-containing solvents were co-intercalated to some extent, one may conclude that SnCl₆²⁻ ions and not SnCl₄ molecules are intercalated in these compounds. Most acceptor GICs contain discrete anions in the intercalated layers. The remaining space is filled with neutral molecules and/or solvent molecules if intercalation occurred from solution. For instance, the composition of stage 1 graphite hydrogensulfate is C₂₄⁺HSO₄⁻ · 2.43 H₂SO₄. Polar molecules may solvate the intercalated ions [9, 10], the energy of solvation contributing to the over-

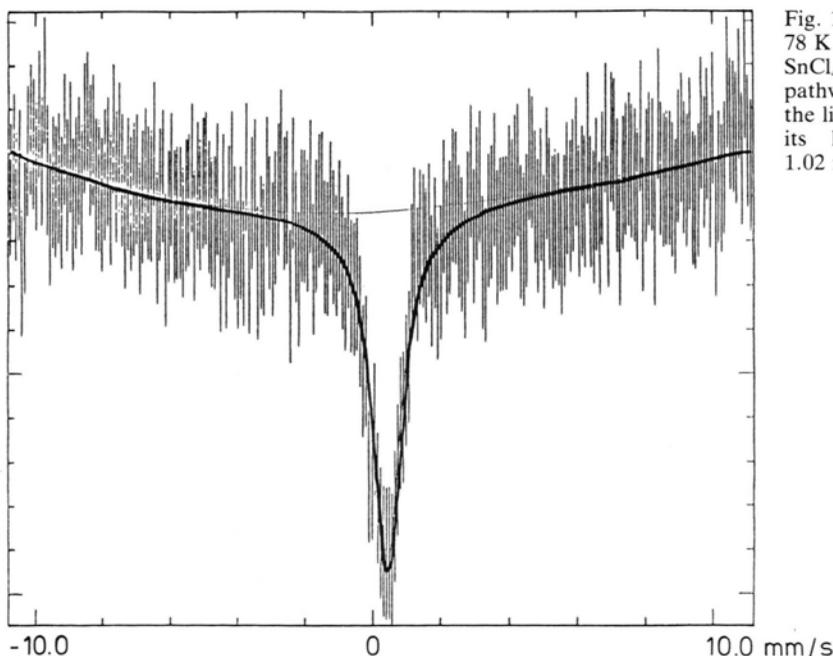


Fig. 1. Mössbauer spectrum at 78 K of the reaction product of SnCl₄ with graphite (reaction pathway 4). The isomer shift of the line is 0.39 mm/s (*vs.* SnO₂), its line width (FWHM) is 1.02 mm/s.

all energy balance. In our case, molecules with a dipole moment could come from the solvent or from photochemical reactions of the solvent.

The presence of SnCl_6^{2-} ions in our compounds is confirmed by their ^{119}Sn Mößbauer spectra (Fig. 1) which show a single, sharp absorption line without any resolvable quadrupole splitting as is expected for cubic symmetry of the ligands around the Sn nucleus. The isomer shift of 0.39 mm/s agrees much closer with that of MgSnCl_6 (0.49 mm/s) than with that of free SnCl_4 (0.83 mm/s). The down-shift by 0.1 mm/s indicates that the s electron density is somewhat in-

creased at the Sn nuclei as a consequence of intercalation. This finding is supported by XPS data [11].

A detailed publication dealing mainly with NMR spectroscopic studies of the new SnCl_4 -GICs is to be published. Trimethyltinchloride, $(\text{CH}_3)_3\text{SnCl}$, has also been successfully intercalated by photochemical reaction [11].

We acknowledge gratefully financial support by the Fonds der Chemischen Industrie. We thank Professor J. M. Thomas of the University of Cambridge for giving us access to his Mößbauer equipment.

-
- [1] A. Hérold, in F. Lévy (ed.): *Intercalated Layered Materials*, Reidel Publ. Comp., Dordrecht, NL (1979), p. 323.
- [2] H. Selig and L. B. Ebert, *Adv. Inorg. Chem. Radiochem.* **23**, 281 (1980).
- [3] M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 139 (1981).
- [4] S. A. Solin, *Adv. Chem. Phys.* **49**, 455 (1982).
- [5] E. Stumpp, *Physica* **105 B**, 9 (1981).
- [6] E. Stumpp and K. Klink, paper presented at the Colloque R. C. P. "Composés Lamellaires" of the C. N. R. S., Les Sables d'Olonne 1982; full publication in print in *Synth. Met.*
- [7] A. Boeck and W. Rüdorff, *Z. Anorg. Allg. Chem.* **397**, 179 (1973).
- [8] R. Schlögl and H. P. Boehm, Preprints, CARBON '80. Internat. Carbon Conf., Baden-Baden (1980), p. 114; detailed publication in preparation.
- [9] F. Béguin, L. Gataineau, and R. Setton, Ext. Abstr., CARBON '82, 6th London Internat. Carbon and Graphite Conf. (1982), p. 97.
- [10] F. Béguin, J. Jegoudez, C. Mazières, and R. Setton, *C. R. Acad. Sci., Paris* **II 293**, 969 (1981); J. Jegoudez, C. Mazières, and R. Setton, *Synth. Met.*, in print.
- [11] R. Schlögl, Dissertation, Univ. München 1983.