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Preparation of Graphite Intercalation Compounds of Thiazyl Salts

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Thiazyl salts prepared from $S_3N_3Cl_3$ and MCl_3(M=Sb, Fe, Al) were intercalated into flaky or powdery natural graphite in CCl_4 or $SOCl_2$. Intercalation compounds prepared are $C_{24}S_4N_4\cdot 2SbCl_5$ [2nd stage, I_c(repeat distance) $=12.81\pm0.02$ Å], $C_{9.5}\cdot 0.2(S_3N_3Cl_3\cdot FeCl_2)\cdot 0.8(SOCl_2\cdot FeCl_2)$ [2nd stage, $I_c=12.77\pm0.03$ Å], $C_{11}S_3N_3Cl_3\cdot 2.4FeCl_2$ [a mixture of 1st and higher stage compounds, $I_c=9.17\pm0.05$ Å] and $C_{24}\cdot 0.4(S_3N_3Cl_3\cdot 2AlCl_2)\cdot 0.6(SOCl_2\cdot 2AlCl_2)$ [a mixture of 2nd and 3rd stage compounds, $I_c=12.89\pm0.03$ Å, 16.23 ± 0.03 Å]. Electrical conductivity of pyrolytic carbon–$S_4N_4\cdot 2SbCl_5$ [3rd stage] is higher than that of original pyrolytic carbon by one order.

In recent years, attention has been given to graphite intercalation compounds showing metallic behavior, *i. e.* high electrical conductivity. Alkali metal, acid or some halide compounds have such properties. Graphite compounds intercalated by strong Lewis acids such as SbF_5, AsF_5 are also of interest.[1] Most chlorides or fluorides of metals in higher oxidation states are hygroscopic and unstable. In many cases, their graphite intercalation compounds also have similar properties. However, such halides are stabilized to some extent forming ionic complexes with anion donor halides. Graphite intercalation compounds of the ternary system might be considered to be effective for preparing stable compounds with high electrical conductivity.

Ternary system compounds were prepared by the reaction of six-membered ring compound $S_3N_3Cl_3$ with metal chlorides ($SbCl_3$, $FeCl_3$, $AlCl_3$) in CCl_4 or $SOCl_2$ containing graphite. Electrical conductivity was measured for a relatively stable compound with pyrolytic carbon host, obtained in a form suitable for measurement.

Experimental

Flaky natural graphite from Madagascar consisting of two different grain sizes of over 500 μm(80%) and 297—500 μm (20%), and powdery natural graphite of less than 44 μm, were used. Purity was 99.4% after purification with a hydrogen fluoride solution. Trithiazyl trichloride $S_3N_3Cl_3$ (yellow crystals, mp 91 °C) was prepared by the usual method.[2] Commercial $SbCl_3$, $FeCl_3$, and $AlCl_3$ were used without further purification. All the reactions were carried out under nitrogen or dry atmosphere. Graphite intercalation compounds prepared were analysed by means of X-ray diffractometry and elemental analysis. The X-ray diffraction pattern for a moisture-sensitive compound was taken by wrapping the sample in thin, transparent poly(vinyl chloride) resin. Elemental analysis was performed at the Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Science, Kyoto University for C, N, Cl, and at Kyoto Science Research Institute of Shimadzu Seisakusho Corporation for Sb, Fe, Al, and S. A-axis electrical conductivity was measured for pyrolytic carbon (PC), PC–$S_4N_4\cdot 2SbCl_5$, and PC–$SbCl_5$ by the 4-point DC-bridge method. The host material was a pyrolytic carbon plate (Nihon Carbon Comp. Ltd.) deposited at 2100 °C and further treated at 2400 °C.

The compounds were prepared as follows.

1) $C_{24}S_4N_4\cdot 2SbCl_5$. Flaky graphite (1.416 g), $SbCl_3$ (4.433 g, 19.4 mmol) and $S_3N_3Cl_3$ (1.589 g, 6.50 mmol) were added to 60 ml of dry CCl_4 in a 100 ml glass flask. The solution was then heated at 55 °C in an oil bath and stirred for 12 d. The reaction was completed in 1—2 h, a red-brown compound being precipitated from the solution. After 3 d, flaky graphite began to expand with insertion of the product. It took over a week for thiazyl salt to be intercalated completely. The product was filtered under nitrogen or dry atmosphere and dried in a vacuum.

2) $C_{9.5}\cdot 0.2(S_3N_3Cl_3\cdot FeCl_2)\cdot 0.8(SOCl_2\cdot FeCl_2)$ *and* $C_{11}S_3N_3Cl_3\cdot 2.4FeCl_2$. Flaky graphite (1.024 g), $FeCl_3$ (2.038 g, 12.60 mmol), $S_3N_3Cl_3$ (1.537 g, 6.28 mmol), and powdery graphite (0.693 g), $FeCl_3$ (1.397 g, 8.50 mmol), $S_3N_3Cl_3$ (1.040 g, 4.25 mmol) were added to 40 ml of $SOCl_2$. Each solution was then heated at 50 °C and stirred for 7 and 8 d, respectively. The compounds were isolated in the same way as for *1)*.

3) Reaction of Flaky Graphite with $S_3N_3Cl_3+2AlCl_3$. Flaky graphite (0.975 g), $AlCl_3$ (1.276 g, 9.57 mmol) and $S_3N_3Cl_3$ (1.170 g, 4.78 mmol) were added to 40 ml of $SOCl_2$. The solution was then heated. The compound was isolated in the same way as for *1)*.

4) PC–$S_4N_4\cdot 2SbCl_5$ *and PC–*$SbCl_5$. PC–$S_4N_4\cdot 2SbCl_5$ was prepared by the same method as for *1)*. PC(1 cm², *ca.* 0.1 cm in thickness) and $SbCl_5$ (70 g) were added to 15 ml of dry CCl_4 in a 100 ml flask. The solution was then heated at 100 °C in oil bath and stirred for 10 d.

Results and Discussion

Intercalation of $S_4N_4\cdot 2SbCl_5$. The reaction of $S_3N_3Cl_3$ with $SbCl_3$ gave two different compounds according to the mole ratio of the reactants: in the 1 : 1 reaction, ten-membered S, N ring compound $S_5N_5\cdot SbCl_6$ was crystallized from acetonitrile in orange color, in the 1 : 3 reaction, eight-membered ring compound $S_4N_4\cdot SbCl_5$ was isolated. The compounds were identified by IR spectra[3,4] and elemental analysis. IR (KBr): s (broad) 1166, s (broad) 1121, m 733, w 681, w 630 and vs 545 cm⁻¹. Elemental analysis: Found: S, 28.6; N, 12.6; Cl, 37.6; Sb, 21.1%. Calcd for $S_5N_5\cdot SbCl_6$: S, 28.4; N, 12.4; Cl, 37.7; Sb, 21.6%.

$$S_3N_3Cl_3 + SbCl_3 \xrightarrow[CH_3CN]{R.T.} S_5N_5\cdot SbCl_6 \qquad (1)$$

IR (KBr): vs 1058, vs 976, s 808, vs 788, w 684, vs 512, m 413 cm⁻¹. Elemental analysis: Found: S, 24.7; N, 11.5; Cl, 36.9; Sb, 24.4%. Calcd for $S_4N_4\cdot SbCl_5$: S, 26.5; N, 11.6; Cl, 36.7; Sb, 25.2%.

$$S_3N_3Cl_3 + 3SbCl_3 \xrightarrow[CH_2Cl_2\text{ or }CCl_4]{R.T.} S_4N_4\cdot SbCl_5 \qquad (2)$$

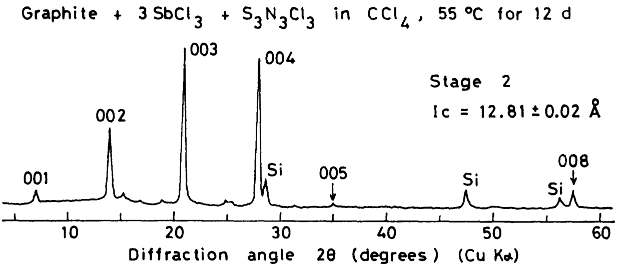

Fig. 1. X-Ray diffraction pattern for $C_{24}S_4N_4 \cdot 2SbCl_5$.

S_5N_5 ring is not as stable as S_4N_4 ring. Repeated recrystallization resulted in the change of the crystal structure from $S_5N_5 \cdot SbCl_6$ to $S_4N_4 \cdot SbCl_5$. When reaction (2) was carried out in the presence of graphite, a brown intercalation compound was obtained after 12 d.

$$\text{Flaky graphite} + S_3N_3Cl_3 + 3SbCl_3 \xrightarrow[CCl_4]{55\,^\circ C} C_{24}S_4N_4 \cdot 2SbCl_5 \qquad (3)$$

The X-ray diffraction pattern for this compound is shown in Fig. 1. The compound was so stable that the diffraction pattern could be taken without wrapping the sample. The repeat distance I_c is 12.81±0.02 Å from the observed (00l) diffraction lines. The result of elemental analysis for this compound coincides with $C_{24}S_4N_4 \cdot 2SbCl_5$. Found: C, 26.6; S, 10.8; N, 4.8; Cl, 32.4; Sb, 21.5%. Calcd for $C_{24}S_4N_4 \cdot 2SbCl_5$: C, 26.9; S, 12.0; N, 5.2; Cl, 33.1; Sb, 22.8%.

In general, the repeat distance of 1st stage compounds of metal chlorides is in the range of 9—10 Å.[5] 1st stage compound $C_{12}SbCl_5$ has 9.42 Å as the repeat distance,[5] indicating that the interlayer spacing of graphite is expanded by 6.07 Å with intercalation of $SbCl_5$. S_4N_4 reacts with metal chlorides ($SbCl_5$, $FeCl_3$, $AlCl_3$ *etc.*) to give mono- and diadducts.[4,8] The intercalant $S_4N_4 \cdot 2SbCl_5$ is regarded as a diadduct of S_4N_4. Considering that the dimension of monoadduct $S_4N_4 \cdot SbCl_5$ is *ca.* 6 Å,[7] it is possible that the intercalant $S_4N_4 \cdot 2SbCl_5$ is oriented between the interlayer spacing of 6.11 Å ($=12.81-3.35\times2$). Thus, $C_{24}S_4N_4 \cdot 2SbCl_5$ is assigned to a 2nd stage compound.

DTA and TG curves of $C_{24}S_4N_4 \cdot 2SbCl_5$ were obtained to determine the decomposition temperature. Decomposition of the intercalant began at *ca.* 150 °C and was completed at *ca.* 250 °C through $S_4N_3Cl \cdot SbCl_3$.

Reaction of Graphite with $S_3N_3Cl_3+2FeCl_3$. $S_3N_3Cl_3$ reacts with $FeCl_3$ to give 1 : 1 or 1 : 2 adduct.[9] In this case, $SOCl_2$ used as a solvent also forms an adduct with $FeCl_3$.[9] When the reaction was carried out in $SOCl_2$ containing flaky graphite, a black intercalation compound was isolated after 1 week. The repeat distance is calculated to be 12.77±0.03 Å from the (00l) diffraction lines shown in Fig. 2. The composition was derived from the elemental analysis as $C_{9.5} \cdot 0.2(S_3N_3Cl_3 \cdot FeCl_2) \cdot 0.8(SOCl_2 \cdot FeCl_2)$. The prepared compound contains much solvent.

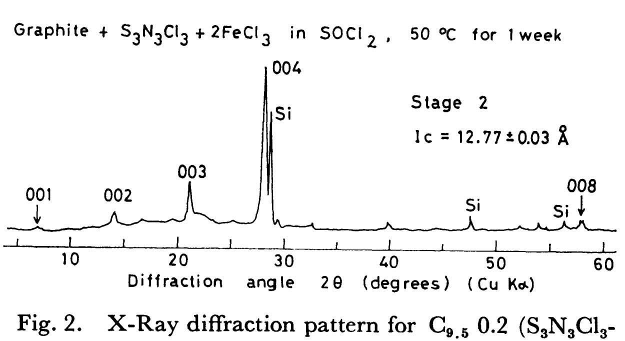

Fig. 2. X-Ray diffraction pattern for $C_{9.5}$ 0.2 ($S_3N_3Cl_3$-$FeCl_2$)0.8($SOCl_2FeCl_2$).

$$\text{Flaky graphite} + S_3N_3Cl_3 + 2FeCl_3 \xrightarrow[SOCl_2]{50\,^\circ C} C_{9.5} \cdot 0.2(S_3N_3Cl_3 \cdot FeCl_2) \cdot 0.8(SOCl_2 \cdot FeCl_2) \qquad (4)$$

Found: C, 29.2; S, 11.6; N, 2.2; Cl, 38.4; Fe, 14.4; (O), 3.5%. Calcd for $C_{9.5} \cdot 0.2(S_3N_3Cl_3 \cdot FeCl_2) \cdot 0.8(SOCl_2 \cdot FeCl_2)$: C, 29.6; S, 11.8; N, 2.2; Cl, 38.6; Fe, 14.5; (O), 3.3%.

$FeCl_2$ forms 1st stage intercalation compound with the composition $C_{4.7}FeCl_2$ and the repeat distance 9.56 Å.[5] The number of carbon is 9.5 per one intercalated molecule, in line with twice that for 1st stage compound. The repeat distance also indicates that the compound is a 2nd stage one.

The compound decomposed on exposure to the air, accompanied by decrease in weight and release of chlorine gas. After being left to stand for several hours, the diffraction lines for initial graphite appeared on the diffraction pattern.

When powdery graphite was used as host material instead of flaky graphite, another intercalation compound $C_{11}S_3N_3Cl_3 \cdot 2.4FeCl_2$ containing no solvent was formed.

$$\text{Powdery graphite} + S_3N_3Cl_3 + 2FeCl_3 \xrightarrow[SOCl_2]{50\,^\circ C} C_{11}S_3N_3Cl_3 \cdot 2.4FeCl_2 \qquad (5)$$

Found: C, 19.9; S, 13.5; N, 6.3; Cl, 41.8; Fe, 18.9%. Calcd for $C_{11}S_3N_3Cl_3 \cdot 2.4FeCl_2$: C, 19.4; S, 14.1; N, 6.2; Cl, 40.6; Fe, 19.7%.

This is also black and a mixture of 1st and higher stage compounds. Powdery graphite has a much greater surface area than flaky graphite. However, no pure 1st stage compound could be obtained. The observed repeat distance for 1st stage compound is 9.17±0.05 Å, and the strong peak at 27.2° corresponds to (00l) line of higher stage compounds (Fig. 3). The characteristic of this compound is similar to that of $C_{9.5} \cdot 0.2(S_3N_3Cl_3 \cdot FeCl_2) \cdot 0.8(SOCl_2 \cdot FeCl_2)$.

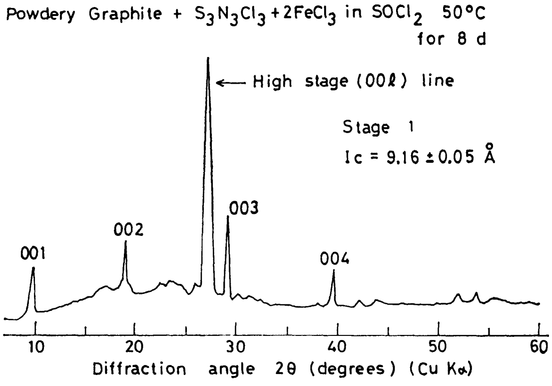

Fig. 3. X-Ray diffraction pattern for $C_{11}S_3N_3Cl_3 \cdot$ $2.4FeCl_2$.

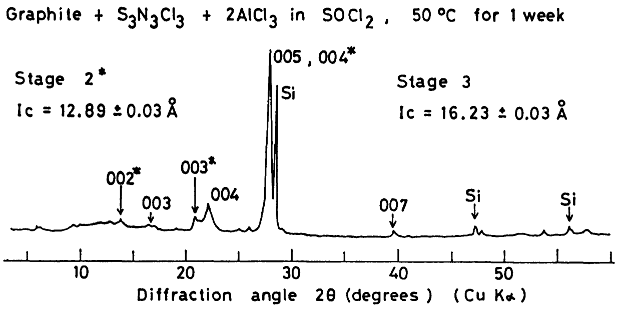

Fig. 4. X-Ray diffraction pattern for $C_{24}\cdot 0.4(S_3N_3Cl_3\text{-}2AlCl_2)\cdot 0.6(SOCl_2\cdot 2AlCl_2)$.

Reaction of Graphite with $S_3N_3Cl_3+2AlCl_3$. $S_3N_3Cl_3$ reacts also with $AlCl_3$ to give 1 : 1 or 1 : 2 adduct.[9] Reaction of flaky graphite with the adduct gave a green-black compound. X-Ray diffraction pattern (Fig. 4) indicates the coexistence of 2nd and 3rd stage compounds. No pure 2nd stage compound was obtained even by the reaction for *ca.* one month. The reaction rate from 3rd stage to 2nd stage might be low in this system. Their repeat distances are 12.89±0.03 Å and 16.23±0.03 Å, respectively. From the elemental analysis, the composition is approximated to $C_{24}\cdot 0.4(S_3N_3Cl_3\cdot 2AlCl_2)\cdot 0.6(SOCl_2\cdot 2AlCl_2)$.

$$\text{Flaky graphite} + S_3N_3Cl_3 + 2AlCl_3 \xrightarrow[SOCl_2]{50\,^\circ C}$$
$$C_{24}\cdot 0\ 4(S_3N_3Cl_3\cdot 2AlCl_2)\cdot 0\ 6(SOCl_2\cdot 2AlCl_2) \quad (6)$$

Found: C, 44.1; S, 9.1; N, 2.2; Cl, 30.7; Al, 7.4; (O), 5.8%. Calcd for $C_{24}\cdot 0.4(S_3N_3Cl_3\cdot 2AlCl_2)\cdot 0.6(SOCl_2\cdot 2AlCl_2)$: C, 44.1; S, 8.8; N, 2.6; Cl, 34.7; Al, 8.3; (O), 1.5%.

A considerable discrepancy exists between analytical and calculated values for chlorine. The compound is very hygroscopic and unstable. As soon as it was taken out from a flask into the air, it decomposed liberating chlorine gas. The color turned from green-black to black. Analytical error occurred probably because of such property. Some unknown peaks appeared on the X-ray diffractogram for a decomposed compound, no peak corresponding to the original graphite being observed. The black substance may be a kind of residual compound.

Electrical Conductivity Measurement. The results of a-axis electrical conductivity for PC, PC–$SbCl_5$, and PC–$S_4N_4\cdot 2SbCl_5$ are given in Table 1. Both PC–$SbCl_5$ and PC–$S_4N_4\cdot 2SbCl_5$ were confirmed to be 3rd stage compounds by means of X-ray diffractometry. The electrical conductivity of PC–$SbCl_5$ and PC–$S_4N_4\cdot 2SbCl_5$ is obviously higher than that for original PC by one order. The chemical bond between S_4N_4 and $SbCl_5$ is the coordination of antimony atom of $SbCl_5$ as a Lewis acid to nitrogen atom of S_4N_4, the intercalant $S_4N_4\cdot 2SbCl_5$ having partially ionic character represented by $S_4N_4{}^{\delta+}\cdot 2SbCl_5{}^{\delta-}$.[7] It is likely that $S_4N_4\cdot 2SbCl_5$ is comparable with $SbCl_5$ in its ability as an electron acceptor which removes an electron from graphite and leaves behind a delocalized hole. Insertion of S_4N_4 increases the stability of the intercalation compound as compared with PC–$SbCl_5$.

TABLE 1. ELECTRICAL CONDUCTIVITIES OF PC, PC–$SbCl_5$, AND PC–$S_4N_4 2SbCl_5$ AT 25 °C

Compound	$\sigma_a/\Omega\ cm^{-1}$
Pyrolytic carbon	3.9×10^3
PC–$SbCl_5$ (3rd stage)	4.1×10^4
PC–$S_4N_4\cdot 2SbCl_5$ (3rd stage)	4.4×10^4

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