

Reaction of Chloroacids with Graphite

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Introduction

Certain metal chlorides combine with hydrochloric acid to form chloroacids. We found that some of these acids are capable to be intercalated into graphite.¹ However, no systematic investigation of this reaction has been reported. This is a preliminary report of a detailed study of using chloroacids as starting materials to prepare the corresponding graphite salts.

Chloroacids always contain water of constitution. Although they are best described as oxonium salts with the formula $[H_3O]^+[MCl_x]^{n-} \cdot zH_2O$, in this paper the formula $H_nMCl_x \cdot yH_2O$ will be used.

The stability of chloroacids varies considerably. $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$, for example, can be isolated as solid compounds with a definite composition, others are known to exist only in the presence of excess hydrochloric acid.

Experimental

Natural graphite from Kropfmühl, Bavaria (S 40, particle size 200–300 μm) was used. The chloroacids of Pt, Au, Ir, Sn, Ti, and I were prepared according to the general methods outlined in the literature.² Several procedures for the preparation of GICs were employed.

Method A. Heating a mixture of the chloroacid and graphite in a stream of chlorine.

Method B. Graphite was stirred in a heated solution of the metal chloride in hydrochloric acid saturated with chlorine.

Method C. Heating graphite with a mixture of $SnCl_4$ or $GeCl_4$, respectively, and hydrochloric acid with a chlorine overpressure.

Results and Discussion

GICs obtained using method A. The reaction conditions are collected in Table 1. It also gives the compositions of typical samples. The C:M ratios referred to in Table 1 are rather uncertain because they were calculated without consideration of the co-intercalated water.

The ratios Cl:M, except in GIC 1 and GIC 5, are somewhat lower than in the pristine chloroacids but higher than in the corresponding metal chlorides. Consequently, these GICs may be regarded as graphite salts in analogy to the GICs of strong oxoacids. GIC 10, however, is more likely $TiCl_3$ -graphite rather than graphite-tetrachlorothallate.

GIC 2 is the first example of a stage 1 of graphite-tetrachloroaurate. The interlayer distance is the same as found in $AuCl_3$ -graphite (stage 1) in which planar

Table 1. Experimental details of intercalation of chloroacids (method A)

starting acid	temp./°C	time/h	C : M : Cl	stage	$I_c/\text{\AA}$	sample no.
$HAuCl_4 \cdot 4H_2O$	100	2	64 : 1 : 4.2	2	10.10	1
	150	6	25 : 1 : 3.9	1	6.74	2
$H_2PtCl_6 \cdot 6H_2O$	150	6	63 : 1 : 5.6	3	15.86	3
	150	6	41 : 1 : 5.6	2	12.53	4
$H_2IrCl_6 \cdot 6H_2O$	100	8	50 : 1 : 6.1	2	12.56	5
	200	8	27 : 1 : 4.2	3	15.62	6
$H_2SnCl_6 \cdot 6H_2O$	45	6	a) : 1 : 5.6	6	26.15	7
	45	16	a) : 1 : 5.3	3	16.10	8
	45	30	a) : 1 : 5.4	4	19.45	9
$HTiCl_4 \cdot 3H_2O$	130	6	22 : 1 : 3.2	2	13.10	10
$HICl_4 \cdot 4H_2O$	60	10	63 : 1 : 3.7	6	26.88	11

a) not determined

Au_2Cl_6 units are oriented parallel to the graphene layers.³ The structure of $\text{HfCl}_4 \cdot 4\text{H}_2\text{O}$ is similar to that of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$. In both acids the anions adopt the square planar structure. Accordingly, the sandwich thickness in GIC 11 is the same as in GIC 2.

GIC 4 was obtained by treatment of GIC 3 a second time with chloroplatinic acid. By this procedure a stage 2 of graphite-hexachloroplatinate has been obtained for the first time.

GICs obtained using method B. Whereas graphite did not react with a mixture of SnCl_4 , HCl , and Cl_2 , intercalation took place if some water was added corresponding to a mole ratio $\text{H}_2\text{O}:\text{HCl}:\text{SnCl}_4 = 3.6:0.8:1$. The upper limit of the water content was found to be 7:2:1. Thus it is reasonably certain that intercalation of SnCl_4 occurs only in the presence of H_3O^+ ions. As in the case of GICs with oxoacids only highly concentrated chloroacids can be intercalated.

The ratios $\text{Cl}:\text{Sn}$ in the GICs varies between $>5:1$ and $4.5:1$. The latter value was found when the reaction time was longer (ca. 6 h). These GICs can be represented by the formula $\text{C}_n\text{SnCl}_6^{2-} \cdot 3\text{SnCl}_4 \cdot y\text{H}_2\text{O}$. Thus the intercalate consists of anions and neutral molecules as in the case of graphite hydrogensulphate. Similar results were obtained by the UV irradiation induced intercalation of SnCl_4 in CCl_4 .⁴ SnCl_4 -GICs obtained with method B gave x-ray patterns corresponding to stage 4 and stage 3 structures.

Chloroacids of HgCl_2 are very unstable. Therefore, mixtures of mole ratio $\text{H}_2\text{O}:\text{HCl}:\text{HgCl}_2 = 4:1:1$ were heated with graphite. The optimum temperature was found to be ca. 90 °C. In all runs stage 3 GICs were obtained ($I_c=16.30$ Å). The ratios $\text{Cl}:\text{Hg}$ depended on the reaction time. After 4 h a value of 2.7:1 and after 200 h of 2.2:1 was found. The primary products seem to be graphite salts which are converted to HgCl_2 -graphite on prolonged treatment with the HCl/HgCl_2 mixture. Residue compounds of graphite nitrate were found to be more reactive than pristine graphite. With residue compounds mixtures of stage 2 and 3 HgCl_2 -GICs were obtained.

FeCl_3 -graphite has been prepared in a solution of FeCl_3 in concentrated hydrochloric acid ($\text{H}_2\text{O}:\text{HCl}:\text{FeCl}_3 = 2.4:0.7:0.4$, 90 °C, 5 h). The GIC was of stage 2 with the composition $\text{C}:\text{Fe}:\text{Cl} = 37:1:3.4$. The x-ray reflexes of GICs prepared in aqueous solutions are considerably broader than those of compounds obtained by the "classical" method.

GICs obtained using method C. The reaction conditions and results are summarized in Table 2.

Table 2. Reaction of mixtures of SnCl_4 and $\text{HCl}(\text{aq})$ with graphite under chlorine overpressure. Reaction time 60 h, temp. 70 °C

starting mixture $\text{H}_2\text{O}:\text{HCl}:\text{SnCl}_4$	ratio $\text{Cl}:\text{Sn}$ in GIC	stage
0 : 0 : 1	no reaction	
8 : 2 : 1	5.02:1	4
5.6 : 1.4 : 1	5.18:1	3
2.8 : 0.7 : 1	5.13:1	3
1.4 : 0.35 : 1	5.00:1	2+3

Again, it was found that intercalation of SnCl_4 takes place only in the presence of a trace of water. In this series of experiments the $\text{Cl}:\text{Sn}$ ratios of the intercalate are fairly constant in spite of changing $\text{Cl}:\text{Sn}$ ratios in the starting mixtures. The intercalate is probably a 1:1 mixture of SnCl_4 and SnCl_6^{2-} .

Russian workers have recently also found evidence for the existence of GICs with SnCl_4 but of general formula C_nSnCl_6 .⁵ Anhydrous stannic chloride has been used and chlorine pressures up to 1.0 MPa.

Method C has been successfully used to prepare also GICs with GeCl_4 for the first time.

Reaction of ether complexes of chloroacids with graphite

MCl_3 ($\text{M}=\text{Al}, \text{Tl}$) react with a solution of HCl in diethyl ether to give compounds of the type $[(\text{Et}_2\text{O})_n\text{H}]^+[\text{MCl}_4]^-$. These acids were heated with graphite in a chlorine atmosphere. The samples were washed with ether. The optimum reaction conditions were (i) with $\text{M}=\text{AlCl}_3$ 90 °C, 14 h; found: $\text{C}:\text{Al}:\text{Cl} = 30:1:3.7$, stage 2; (ii) with $\text{M}=\text{TlCl}_3$ 80 °C, 15 h; found: $\text{C}:\text{Tl}:\text{Cl} = 16:1:3.4$, stage 1. The analytical data indicate that these GICs are also graphite salts.

Intercalation of AlCl_3 was also observed in molten $\text{AlCl}_3 \cdot 2 \text{EtO}$, that is in the absence of HCl . The presence of Cl_2 is necessary. Found: $\text{C}:\text{Al}:\text{Cl} = 30:1:3$, stage 3.

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