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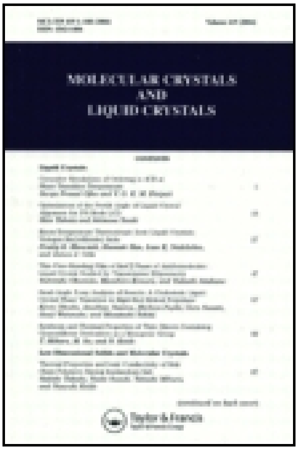

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XAS AND XRD STUDIES ON GRAPHITE INTERCALATION COMPOUNDS OF H_2PtCl_6

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Abstract Graphite intercalation compounds (GICs) of H_2PtCl_6 were studied using X-ray diffraction and X-ray absorption (XAS) methods. Particularly, the results will be interpreted in correlation to charge transfer. For the orthogonal in-plane lattice following parameters are found: a = 2024 pm, b = 1353 pm, and $\gamma = 90^\circ$. The analysis of the EXAFS at the Pt L_{III} edge yields a slightly decreased Pt-Cl bond length and additionally coordinated Cl atoms in comparison to the pure compound. This is in agreement with results evaluated from the Cl K edge. A small energy shift of 0.25 eV of the Pt L_{III} edge to higher energies excludes a charge transfer to Pt in the intercalate.

INTRODUCTION

A correlation between charge transfer and bond length in acceptor GICs was implied in several works. For ICl-GIC, e. g., an increase of the I-Cl distance was found.[1] But in some compounds factors other than charge transfer seem to dominate. So in $ZnCl_2$-GIC a decrease in bond length results from geometrical alteration.[2] The following study will give a further contribution to this and related questions.

EXPERIMENTAL

We used natural graphite flakes (Kropfmühl/Germany) with diameter 600-800 μm. $H_2PtCl_6 \cdot 6H_2O$, K_2PtCl_6, and $PtCl_2$ were purchased from Aldrich. The preparation of the H_2PtCl_6-GICs was carried out in sealed ampoules containing 15 bar chlorine. The ampoules were inserted in a steel container and heated in an one temperature furnace at 150° C for seven days. First a compound with stage 2.2 was obtained

(H_2PtCl_6 - GICl). The GIC was subsequently heated in a nitrogen flow at 225° C (H_2PtCl_6-GIC2) and at 240° C (H_2PtCl_6-GIC3) to remove water and hydrochloric acid.[3] All samples were characterized by 001 diffractograms. The stage number increased from 2.2 to 2.6 (GIC2) and 3.0 (GIC3), respectively. The monochromatic Laue method was applied to evaluate the in-plane lattice of the intercalate.

The XAS measurements were performed at HASYLAB/Hamburg . The Pt L_{III} edge was measured using the RÖMO II beamline and the Cl K edge using the EXAFS II beamline. The energy of the Pt L_{III} edge (E = 11.5637 keV) was calibrated against W L_{II} edge (E = 11.528 keV), the energy of the Cl K edge (E = 2.822 keV) against the Ar K edge (E = 3.202 keV). The samples were prepared as polyethylene pellets in a glove box.

RESULTS AND DISCUSSION

The monochromatic Laue photographs and the evaluated hk0 diffraction pattern of the GICs are shown in Figure 1 and 2. Both the thermical treated and the parent GIC reveal the same orthogonal in-plane lattice with following parameters:

$$a = 2024 \text{ pm},\ b = 1353 \text{ pm},\ \gamma = 90°,\ \text{and}\ \delta_a = 30° .$$

δ_a denotes the angle between the graphite and the intercalate a-axes. In H_2PtCl_6-GIC3 the reflections of this lattice become diffuse indicating progressing disorder due the thermical treatment. The H_2PtCl_6-GIC1 shows additional reflections, and in all compounds some further unidentified reflections are observed. It is noticeable that the lattice parameter a is twice that of the pristine K_2PtCl_6 (a = 975 pm).[4]

The Pt L_{III} absorption edges of the H_2PtCl_6-GICs and reference compounds (Figure 3) were determined in two different ways, first as the inflection point of the absorption edge and second by fitting the white line with a Lorentzian function. Relative to the lowest oxidation state of Pt ($PtCl_2$), the energy shift of the measured compounds is shown in Table 1. In comparison to pure $H_2PtCl_6 \cdot 6H_2O$, the GICs exhibit a small energy shift of 0.25 eV to higher energies indicating that there is no chemical reduction of Pt as a result of charge transfer. Additionally, an 18 % increase of the area under the white line of the GICs indicates that the electron density is subtracted from the Pt atoms. The Fourier transforms (FTs) of the EXAFS at the Pt L_{III} edge are shown in Figure 4. Conventional data evaluation procedures were applied to isolate phase and amplitude functions from K_2PtCl_6. In this compound the Platinum atom is octahedrally coordinated to six chlorine atoms with a bond length

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of 233 pm.[4] The results of the fit of the Fourier filtered first coordination shell of H_2PtCl_6-GICs are listed in Table 2. It is evident that the H_2PtCl_6-GIC2 and GIC3 does not show the expected change to $PtCl_4$-GIC with tetrahedrally coordinated Pt atom. This result is in agreement with the analysis of the hk0 diffraction pattern mentioned before. Moreover, the increased coordination number of Pt in the GICs suggests that additional coordinating Cl atoms receive charge transferred from the graphite.

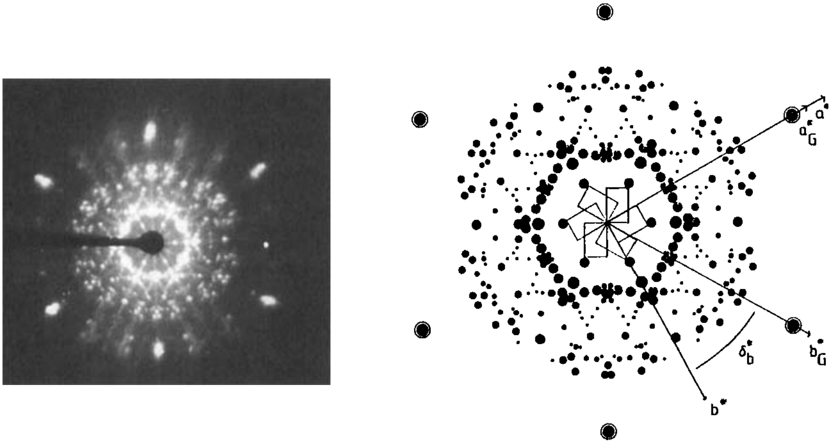

FIGURE 1 (a) Monochromatic Laue photograph of H_2PtCl_6-GIC1. (b) hk0 diffraction pattern as evaluated from (a), one unit cell for each of the six possible rotational positions is depicted.

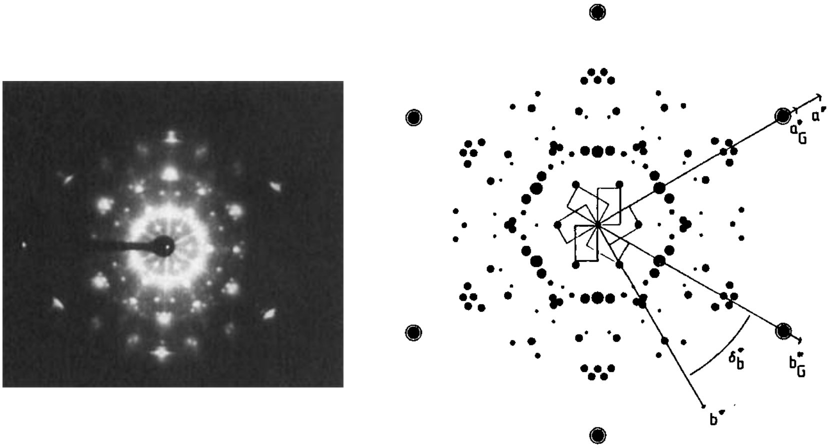

FIGURE 2 (a) Monochromatic Laue photograph of H_2PtCl_6-GIC2. (b) hk0 diffraction pattern as evaluated from (a).

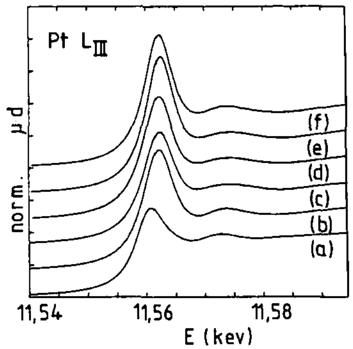

FIGURE 3 XANES spectra at the Pt L$_{III}$ edge of (a) $PtCl_2$, (b) $PtCl_4$, (c) K_2PtCl_6, (d) $H_2PtCl_6 \cdot 6\ H_2O$, and (e) H_2PtCl_6-GICl.

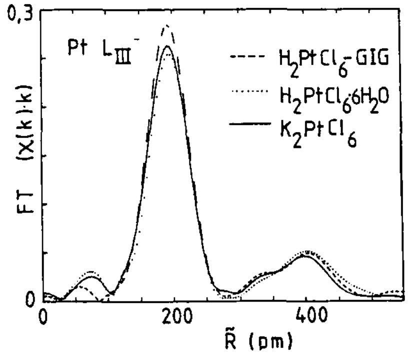

FIGURE 4 FTs of the EXAFS spectra (modified radial distribution function) at the Pt L$_{III}$ edge.

TABLE 1 Energy of the Pt L$_{III}$ edge relative to $PtCl_2$ determined by the inflection point of the absorption edge $\Delta E_0(1)$ and by fitting the white line with a Lorentzian function $\Delta E_0(2)$.

	$\Delta E_0(1)$ (eV)	$\Delta E_0(2)$ (eV)
H_2PtCl_6-GICl,2,3	1.75	1.85
$H_2PtCl_6 \cdot 6\ H_2O$	1.5	1.6
K_2PtCl_6	1.5	1.6
$PtCl_4$	1.2	1.5
$PtCl_2$	0	0

TABLE 2 Coordination number N, bond length R, Debye-Waller factor $\Delta\sigma^2$ obtained from the fit of the first shell of H_2PtCl_6-GICs in comparison to K_2PtCl_6.

	N	R (pm)	$\Delta\sigma^2$ (pm^2)
K_2PtCl_6	6.0	233	0
$H_2PtCl_6 \cdot 6\ H_2O$	6.0	233	0.4
H_2PtCl_6-GIC1	6.7	232	5.0
H_2PtCl_6-GIC2	6.6	232	20
H_2PtCl_6-GIC3	6.6	232	20

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The XANES spectra of the GICs and the pure compounds at the Cl K edge are shown in Figure 5. Peak A is due to the electronic transition from the Cl 1s level to an empty, antibonding MO (σ^*). Peak B and C may be caused by transitions to high-lying empty MOs which are composed of overlapping Pt 5d and 6p orbitals with Cl 4p orbitals.[5] The intensity of Peak C becomes smaller in comparison to the pristine compounds. Furthermore, this peak is broader and shifted to higher energies about 0.4 eV. The intensity of Peak A decreases about 45 %. This can be ascribed to a charge transfer to the Cl atoms in the H_2PtCl_6-GIC. In contrast to the sharp Peak A′ of the GIC in $H_2PtCl_6 \cdot 6\ H_2O$ only a shoulder can be observed indicating an alteration of the band structure, too.

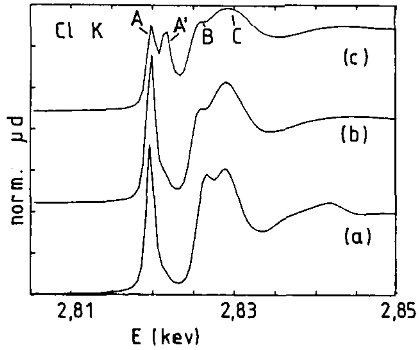

FIGURE 5 XANES spectra at the Cl K edge of (a) K_2PtCl_6, (b) $H_2PtCl_6 \cdot 6\ H_2O$, and (c) H_2PtCl_6-GICl.

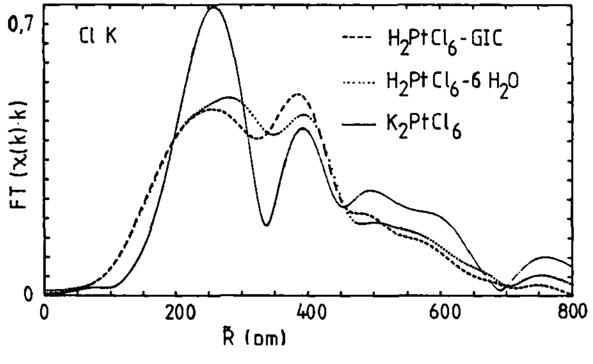

FIGURE 6 FTs of the EXAFS spectra at the Cl K edge. The first coordination shell can be ascribed to the Cl-Pt, the second to the Cl-Cl and K-Cl coordination.

The FT of the Cl K EXAFS (Figure 6) corresponds with the results from the analysis of the EXAFS at Pt L_{III} edge: in both cases a slight decrease of Cl-Pt bond length for the GICs is found. The smaller coordination number of Pt in the first shell fits the increased coordination number of Cl, yielded from the Pt L_{III} edge. Furthermore, the excess chlorine as found from evaluation of the Pt L_{III} edge can also be seen in the second shell of the FT of the Cl K edge.

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