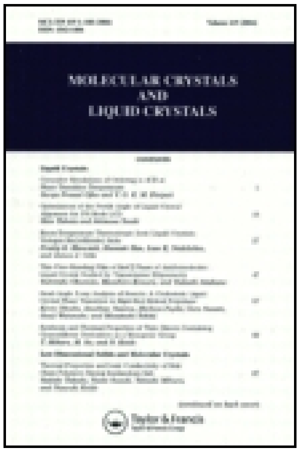

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Eberhard Stumpp [a] & Claus Ehrhardt [a]

[a] Technische Universität Clausthal, Institut für Anorganische Chemie, 38670, Clausthal-Zellerfeld, Germany

Version of record first published: 04 Oct 2006

To cite this article: Eberhard Stumpp & Claus Ehrhardt (1998): Study of the Co-intercalation of Lanthanide Chlorides and Yttrium Chloride into Graphite, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 75-80

To link to this article: http://dx.doi.org/10.1080/10587259808045317

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 75–80
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Study of the Co-intercalation of Lanthanide Chlorides and Yttrium Chloride into Graphite

EBERHARD STUMPP and CLAUS EHRHARDT
Technische Universität Clausthal, Institut für Anorganische Chemie,
38670 Clausthal-Zellerfeld, Germany

Graphite intercalation compounds (GICs) with the trichlorides of Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu have been prepared and characterized by chemical analysis and X-ray diffraction. Attempts to synthesize binary GICs with $LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$ failed. By heating mixtures of YCl_3 + $LnCl_3$ (Ln = La - Lu) with graphite ternary GICs were obtained. The molar ratios $LnCl_3$:YCl_3 in the GICs were found to increase from La to Dy which runs parallel to the decrease in the ionic radii of the Ln^{3+} ions.

Keywords: Graphite intercalation compounds; lanthanide trichlorides

INTRODUCTION

While the chemical properties of anhydrous lanthanide trichlorides (abbreviated $LnCl_3$) are essentially similar, this is not the case for their structural properties. The steady fall in ionic radius along the lanthanide series ("lanthanide contraction") has the effect that different crystal structures occur for different parts of the lanthanide trichlorides. $LaCl_3$-$GdCl_3$ have the hexagonal UCl_3 structure in which each Ln^{3+}-ion is surrounded by approximately nine equidistant chloride ions. The coordination group of the metal ion is a tricapped trigonal prism as shown in Fig. 1.

$TbCl_3$ adopts the $PuBr_3$ structure in which the metal ions are 8-coordinated. The structures of $LaCl_3$ - $TbCl_3$ are therefore spatially cross-linked (3D structures).

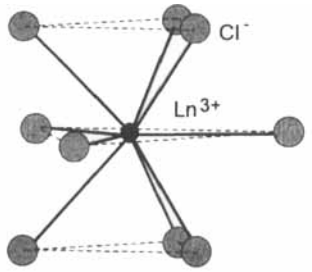

FIGURE 1. Coordination polyhedron of the $LaCl_3$ structure

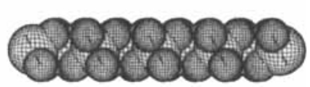

FIGURE 2. Single layer of the YCl_3 structure

$DyCl_3$-$LuCl_3$ differ in structure from the lighter $LnCl_3$. They crystallize in a layer structure and are isostructural with YCl_3. A sheet of this structure may be regarded as a close packing of two layers of chloride ions in which the Ln^{3+} occupy octahedral sites. The side view of such a "sandwich layer" is shown in Fig. 2.

The radius of Y^{3+} lies close to that of the higher Ln^{3+} ions and therefore the chemical properties of yttrium resemble that of the lanthanides, so YCl_3 is also considered here.

Graphite intercalation compounds (GICs) have been prepared with over 40 metal chlorides[1]. They are almost all metal chlorides adopting a layer structure. It was therefore expected that the $LnCl_3$ with the YCl_3 structure were capable of forming GICs. Indeed in a previous study we have prepared GICs with $DyCl_3$ through $LuCl_3$ and, surprisingly, also with $SmCl_3$, $EuCl_3$, $GdCl_3$, and $TbCl_3$[2]. To enhance the intercalation rate of these chlorides it was found advantageous to use Al_2Cl_6 vapor to form gaseous complexes with lanthanide chlorides, but this procedure has the disadvantage that a certain amount of $AlCl_3$ is co-intercalated. All attempts to prepare GICs with the UCl_3 structure type trichlorides of La - Nd failed.

In this contribution we report the results of a more thorough reinvestigation of the reactions of $LnCl_3$ with graphite. Homogeneous GICs could be obtained without the addition of $AlCl_3$ as an auxiliary agent. In accordance with the former results only GICs with the chlorides of Sm-Lu could be prepared. This failure prompted us to explore the possibility to prepare co-intercalation compounds (C-GICs) of these chlorides with those $LnCl_3$ which form GICs. Herein we describe C-GICs prepared by the treatment of mixtures of $LnCl_3$ and YCl_3 with graphite.

EXPERIMENTAL SECTION

General Preparative Techniques.

Natural graphite flakes (particle size ca. 0.2 mm) from Kropfmühl, Bavaria, were used.

Method I. Hydrated $LnCl_3$ were prepared by dissolving the oxides in hydrochloric acid. The appropriate $LnCl_3 \cdot 6\text{-}7\ H_2O$ was mixed with graphite and transferred in a silica boat. This was inserted into a fused quartz tube. To dehydrate the hydrated chloride the mixture was heated in an HCl gas stream. The temperature was raised slowly to about 300 °C and then maintained for 5 hours. To prepare the GIC the HCl gas stream was displaced by a chlorine stream and then the graphite-$LnCl_3$ mixture was heated at 600 °C for 5 days. After reaction the samples were washed with hydrochloric acid to remove the $LnCl_3$ which had not reacted. To prepare co-intercalation compounds the starting material was a mixture of the specific lanthanide oxide and Y_2O_3.

Method II. In this method the anhydrous lanthanide chloride was obtained directly from the oxide. A mixture of the particular lanthanide oxide and graphite was heated in a Cl_2 gas stream at 800 °C. In this reaction graphite acts as a reducing agent. After 2 days the temperature was lowered to 600 °C and the heating was continued for 18 days.

The samples were analyzed for Ln and Cl by the pyrohydrolysis method. The compositions of the C-GICs were determined by X-ray fluorescence analysis (XFA). In addition, the samples were combusted. From the mass of the remaining oxide and with the data of the XFA the molar ratio (Ln+Y):C was calculated.

RESULTS AND DISCUSSION

The compositions of representative binary $LnCl_3$-GICs and X-ray data are listed in Table 1.

TABLE 1 Analytical and X-ray data of $LnCl_3$-GICs

Ln	molar ratio C : Ln : Cl	stage	d_i [pm]
Y	18 : 1 : 3.25	2	1286
Sm	35 : 1 : 3.24	4	1973
Eu	28 : 1 : 3.28	3	1640
Gd	19 : 1 : 3.24	2	1298
Tb	18 : 1 : 3.29	2	1287
Dy	17 : 1 : 3.21	2	1291
Ho	17 : 1 : 3.16	2	1290
Er	20: 1 : 3.33	2	1290
Tm	23 : 1 : 3.19	3	1620
Yb	24 : 1 : 3.17	3	1623
Lu	34 : 1 : 3.23	4	1958

Although the chlorides of Sm, Eu, Gd, and Tb do not adopt the YCl_3-structure in the pristine state, they form GICs. The marked similarities of the X-ray diffractograms of YCl_3-GIC and $GdCl_3$-GIC let us assume that in all binary $LnCl_3$-GICs the intercalated $LnCl_3$ adopt a layer structure as shown in Fig. 2. In this arrangement the Ln^{3+} is coordinated by 6 Cl^- ions. Obviously, the Ln^{3+} ions do not tolerate this coordination for radius ratios Ln^{3+}/Cl^- exceeding that of Sm^{3+}/Cl^- = 0.52. Of the structures of the $LnCl_3$, the YCl_3 type structure is packed least efficiently. The $LnCl_3$ which are located near the borders of the structure regions exhibit polymorphism. Under high pressure the YCl_3-type $LnCl_3$ are transformed into the more densely packed $PuBr_3$ structure[3]. The change from the 3D orientation in the pristine chloride to a 2D arrangement in the intercalate may be regarded as caused by a release of pressure.

The results of the co-intercalation experiments are summarized in Table 2.

TABLE 2. Compositions of ($LnCl_3$+YCl_3)-GICs

Ln in YCl_3	molar ratio Y : Ln	molar ratio C : (Ln+Y) : Cl	stage	d_i [pm]	method
La	13.5 : 1	28 : 1 : 2.96	3	1628	I
La	19 : 1	25 : 1 : 3.08	2	1298	II
Ce	9.3 : 1	23 : 1 : 3.12	3	1623	I
Ce	10 : 1	19 : 1 : 3.16	2	1293	II
Pr	4.2 : 1	24 : 1 : 3.14	3	1626	I
Pr	4.9 : 1	18 : 1 : 3.28	2	1289	II
Nd	3.3 : 1	21 : 1 : 3.17	3	1629	I
Nd	4.9 : 1	18 : 1 : 3.28	2	1289	II
Sm	2.0 : 1	18.6 : 1 : 3.28	2	1297	I
Eu	2.0 : 1	16.6 : 1 : 3.18	2	1288	I
Gd	1.4 : 1	18.9 : 1 : 3.22	2	1296	I
Tb	1.3 : 1	19.2 : 1 : 3.18	2	1287	I
Dy	1.0 : 1	18.3 : 1 : 3.18	2		I
Ho	1.2 :1	20.3 : 1 : 3.16	2		I
Er	1.3 : 1	20.8 : 1 : 3.05	2		I
Tm	1.3 : 1	25.3 : 1 : 3.12	2		I
Yb	1.6 : 1	22.1 : 1 : 3.17	2		I
Lu	1.9 : 1	24.8 : 1 : 3.28			I

As expected the $LnCl_3$ (Ln = Sm - Lu) are co-intercalated together with YCl_3. All these GICs proved to be stage 2 compounds although some of the binary GICs have a stage 3 or 4 structure. The amount of co-intercalated $LnCl_3$ seems to depend on the radius of the particular $LnCl_3$. Deviations from the radius of Dy^{3+} in both directions result in a decrease of the ratio $LnCl_3/YCl_3$ as well as in the amount of $LnCl_3$ + YCl_3.

The chlorides of La through Nd which do not form binary GICs are co-intercalated together with YCl_3. In the direction in which the radius ratio Ln^{3+}/Y^{3+} decreases from La^{3+} to Nd^{3+} both the amount of co-intercalated $LnCl_3$ and $LnCl_3$ + YCl_3 increases. It should be noted that samples prepared using method I have a stage 3 structure whereas samples obtained by method II are ($LnCl_3$+YCl_3)-GICs of stage 2 structure. In addition, these samples contain more $LnCl_3$ + YCl_3 than those prepared by method I.

Figure 3 shows the ratios Y:Ln of (YCl_3+LnCl_3)-GICs and the ratios C:Ln of binary $LnCl_3$-GICs. Both curves show minima at Dy.

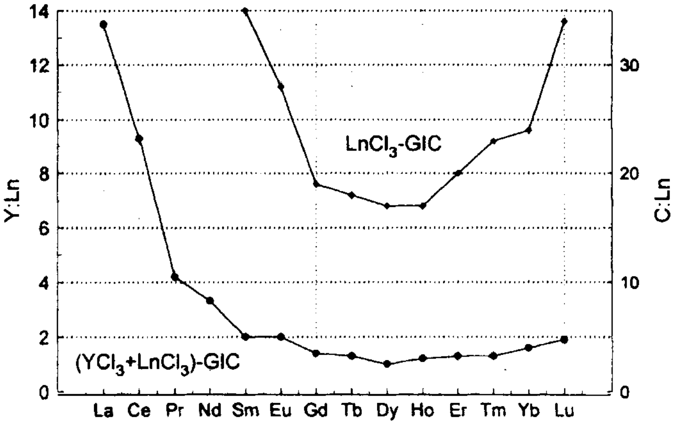

FIGURE 3. Ratios Y:Ln in (YCl_3+LnCl_3)-GICs and ratios C:Ln in $LnCl_3$-GICs

There are very few structural investigations concerning $LnCl_3$ - $Ln'Cl_3$ systems with two different lanthanide ions. Systems in which both chlorides adopt the same structure type usually exhibit continuous solid solution. Phase diagrams were reported for Ln - Ln' = Tb - Dy and Tb -Ho which represent $PuBr_3$-type - YCl_3- type systems[4]. The $PuBr_3$-type structure of the solid solution transforms into the less efficiently packed YCl_3 structure at elevated temperatures. Based on the intercalation experiments it is concluded that a YCl_3 sandwich layer between the graphene sheets can incorporate a small amount of the lighter lanthanide ions.

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