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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Version of record first published: 23 Oct 2006.

To cite this article: Volker Kaiser , Eberhard Stumpp & Beate Tanneberg (1994): Structural studies on Metal Bromide Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 293-298

To link to this article: http://dx.doi.org/10.1080/10587259408050120

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 293–298
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Printed in the United States of America

STRUCTURAL STUDIES ON METAL BROMIDE GRAPHITE INTERCALATION COMPOUNDS.

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ABSTRACT

Some improved X-ray diffraction techniques applied to the two 3rd stage metal bromide graphite intercalation compounds with $CdBr_2$ and $CoBr_2$ should give some more detailed structure informations. However only few more informations have been obtained from precession photographs and high resolution powder diffraction on the two GICs. Measuring several flakes on an automatic four circle diffractometer did not yield additional informations. Some attempts to solve the structure by Rietveld-Methodes using the powder diffraction intentisities failed. Using the few available informations, an idealized model for a 3rd stage GIC is proposed. On the basis of this model some observations are discussed.

INTRODUCTION

The two 3rd stage metal bromide graphite intercalation compounds (GICs) with $CdBr_2$ and $CoBr_2$ have been examined with different X-ray diffraction methods. Several flakes of the two compounds have been investigated on a precession camera with Mo-Kα radiation. Powder samples of each compound have been investigated on a high resolution powder diffractometer (Guinier technique) with Cu-Kα1 radiation. For each compound two types of reflections were determined. There were observed strong and sharp reflexions of a nearly unchanged graphite lattice for both GICs. The broad reflections of the intercalate lattice show that there is only a small sphere of orientated metal bromide. The interpretations of the precession photographs of the two GICs show the same connection between the graphite and the intercalate lattices. The lattices of the two intercalated substances are hexagonal, but twisted by 30° relative to the graphite lattice. The lattice constants were determined to be a=3.97, c=16.22 Å for the Cd-compound, and a=3.79, c=16.49 Å for the Co-compound. Using these values the layer distance for a 3rd stage GIC is calculated to be 9.51 Å for the Cd-compound, and 9.79 Å for the Co-compound. These observations are in good agreement with those found in[1].

An idealized model is supposed for calculating powder patterns and for graphic representations.

EXPERIMENTAL

Sample preparation:

$CdBr_2$-GIC : $CdBr_2$-GIC is obtainable by heating up a mixture of $CdBr_2$ (in excess), graphite and Br_2 in a sealed ampoule for 5 days at 500°C. The product was washed with water and acetone and then dried at 100°C.

$CoBr_2$-GIC : This compound is only obtainable by exchange of $CdBr_2$ with $CoBr_2$ annealing the $CdBr_2$-GIC, $CoBr_2$ (in excess) and Br_2 at 500°C for 5 days. The purification procedure is the same as for the Cd-compound.

Precession photographs on the samples:

Several flakes of the two GICs (0.2 * 0.2 * 0.05 mm) have been given into glas capillars and mounted on a Buerger precession camera (HUBER). After orientating the flakes (parallel and perpendicular to the c-direction) layer photographs (12 - 30 h) have been taken, using MoKα radiation.

Powder diffraction on the samples:

For the powder diffraction patterns (Fig.1) on the two GIC compounds a high resolution Guinier diffractometer has been used. To reduce preferential orientation of the sample, the flakes have been powdered on a greased sample holder. The intensities were measured in steps of 0.04° 2Θ in the range of 2.3° < 2Θ < 100°. The counting time per step was 100 seconds to obtain a good statistic. In table 1 the 2Θ values for the observed reflections and their indexing for the different lattices are given.

RESULTS AND DISCUSSION

For the two GICs of $CdBr_2$ and $CoBr_2$ comparable precession photographs have been obtained. Both compounds show weak reflections of nearly unchanged graphite besides strong and broad reflections of the intercalate lattice in hk-layer photographs. Perpendicular to the c-axis there are only few, very broad reflections besides strikes, which points out that there is an incomensurable modulation along this direction.

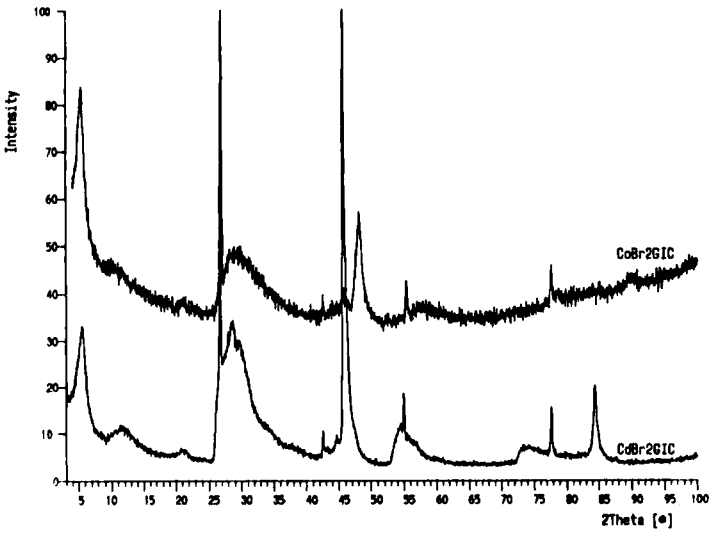

FIGURE 1 Observed powder patterns of the two MBr_2-GICs (Cu Kα1)

TABLE 1 2Θ values and indexing (attachment) for the different lattices of the observed reflexions .

$CdBr_2$-GIC					$CoBr_2$-GIC					
2Θ[°]	d[Å]	h	k	l	2Θ[°]	d[Å]	h	k	l	attached to
5.45	16.23	0	0	1	5.35	16.49	0	0	1	intercalate
11.42	7.93	0	0	2	11.00	8.03	0	0	2	intercalate
21.30	4.16	0	0	4	21.00	4.23	0	0	4	intercalate
26.65	3.34	0	0	2	26.84	3.32	0	0	2	graphite
28.43	3.14	1	0	2	29.20	3.06	1	0	2	intercalate
42.48	2.13	1	0	0	42.44	2.13	1	0	0	graphite
44.59	2.03	0	0	8	45.62	1.99	0	0	8	intercalate
45.62	1.99	1	1	0						intercalate
					48.10	1.89	1	1	1	intercalate
54.40	1.67	2	0	2						intercalate
54.88	1.67	0	0	4	55.38	1.66	0	0	4	graphite
73.28	1.29	1	0	12	57.80	1.59	1	0	9	intercalate
77.62	1.23	1	1	0	77.61	1.23	1	1	0	graphite
84.24	1.15	0	0	14	90.00	1.09	0	0	15	intercalate

The two different lattices of the graphite and the intercalation compound are twisted about 30° against each other. This way of twisted connection between graphite and the intercalate is in agreement with observations on MCl_2-GICs[2]. Since the preferential orientation was reduced in the powder diffraction experiments, much more reflections were obtainable in the two patterns shown in Figure 1. Also using this diffraction technique two types of reflections have been found: there are sharp reflections attached to a nearly unchanged graphite lattice and broad reflections of the intercalate lattice.

Trying to solve the structures by Rietveld methods using the two powder patterns failed, because the reflections of the intercalate lattices are too broad for profile fitting. Using an idealized model of a 3rd stage GIC (Fig.2) powder patterns were calculated (LAZYPULVERIX[3]) for the two compounds. The atomic parameters for this model are given in Figure 2 and Table 2. Because of group - subgroup relations the trigonal space group P321 (No.150[4]) is used. This space group is an acentric non-isomorphic subgroup of P-3m1 (No.164[4]), which is the common subgroup of graphite ($P6_3/mmc$) and $CdBr_2$ (R-3m).

The comparison between observed and calculated intensities (Fig. 3) does not fit very well. There are too many parameters indefinite to obtain a better fit. The idealized model can give only a first starting-point for structure calculations.

The main problem is the structure of the graphite layers inside the bigger (intercalate) unit cell. Using atom positions for an undistorted graphite hexagon leads to significant shorter atomic distances (1.32 Å, 1.27 Å). The normal atomic distance C-C of 1.42 Å does not agree with the intercalate unit cell. The graphite and the intercalate layer must be translationally incommensurate.

TABLE 2 Combination of parameters for the two GICs. Hexagonal setting (lattice constants a, c). C-C layer distance is set to 3.35 Å (parameter v). All distances (dist.) in Å. Parameters u and v are fractional.

GIC	a	c	v	u	M-Br dist.	C-C dist.
$CdBr_2$	3.97	16.22	0.2934	0.09	2.72	1.32
$CoBr_2$	3.79	16.49	0.2968	0.09	2.64	1.26

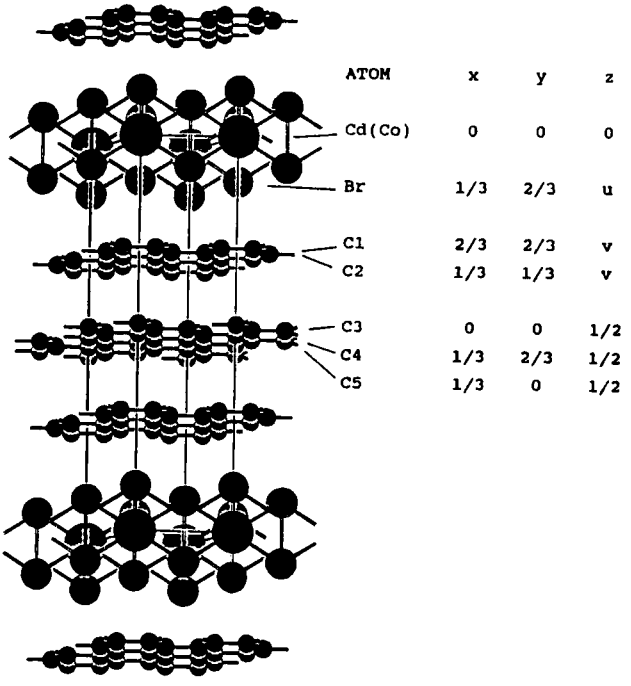

FIGURE 2 Idealized model of a 3rd stage GIC. The atomic positions are related to space group P321 (No.150) and the corresponding lattice constants are given in Table 2.

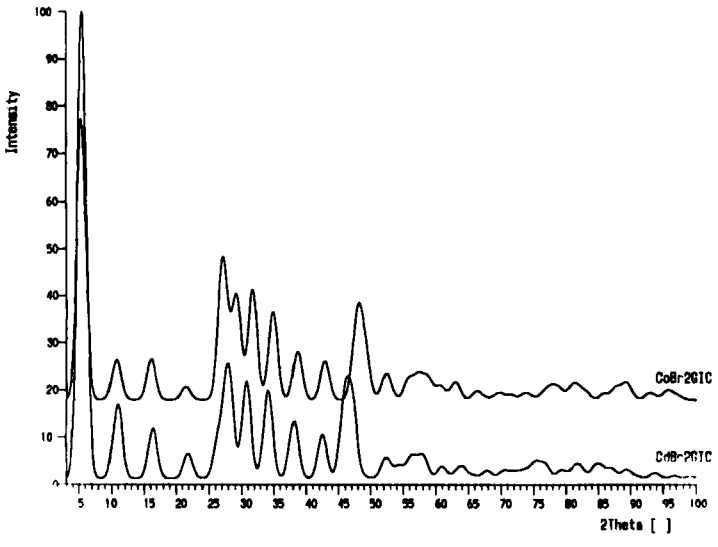

FIGURE 3 Calculated powder patterns of the two GICs, based on the idealized model. The half-wide parameter of the gauss profile has been set to 0.99° 2Θ.

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