In Situ X-Ray Observation on the Intercalation of Weak Interaction Molecules into Perovskite-Type Layered Crystals $(C_9H_{19}NH_3)_2PbI_4$ and $(C_{10}H_{21}NH_3)_2CdCl_4$

Yuri I. Dolzhenko,† Tamotsu Inabe, and Yusei Maruyama*
†Department of Physical Chemistry, Kharkov Polytechnical Institute, Kharkov, 310002, U.S.S.R.
Department of Molecular Assemblies, Institute for Molecular Science, Myodaiji, Okazaki 444

(Received August 5, 1985)

The intercalation-deintercalation process of weak interaction organic molecules such as 1-chloronaphthalene and *o*-dichlorobenzene into highly oriented polycrystalline $(C_{10}H_{21}NH_3)_2CdCl_4$ films and hexane into $(C_9H_{19}NH_3)_2PbI_4$ single crystals has been observed in situ by using X-ray technique. The process is highly reversible. Increasing of interlayer spacing is in reasonable agreement with the size of the intercalated molecules and corresponds to the parallel orientation of aromatic ring planes or hexane chains in between two paraffin layers of the host crystals.

Intercalation phenomena of layered compounds have been known for a long time, and a considerable variety of host lattices that can incorporate atomic or molecular guest species have been investigated, e.g. graphite, clay minerals, layered cyanides, layered dichalcogenides and so on.[1] The attention paid to these compounds began to grow significantly about fifteen years ago, when it was found that some physical properties of layered materials, for example such as superconductivity or cooperative lattice distortions, etc., can be modified significantly by intercalation.[2] On the other hand, intercalated phases show potential technological significance. Their application as reversible electrodes for high-energy-density batteries,[3] and their efficiency as heterogeneous catalysts[4] are well known.

Both academic and technological aspects of intercalation chemistry stimulate an effort to understand the structure, bonding and formation of these compounds in more detail and attempts to synthesize new layered materials and intercalation compounds with interesting structures and properties. During the past few years the range of layered compounds which can be intercalated has been extended to such materials as the almost insulating semiconductor, PbI_2,[5,6] metallic and electron donor type lattice, Ag_2F,[7] black phosphorus (which has both electron-donating and accepting potentiality),[8] and others.[1]

Possible new candidates for intercalation process studies are perovskite-type layered structures of the general formula, $(C_nH_{2n+1}NH_3)_2MCl_4$, where M=Cu^{2+}, Mn^{2+}, Cd^{2+}, Fe^{2+}, Pd^{2+}, Co^{2+}, or Zn^{2+}. Great interest has been shown in these compounds during the past decade since they exhibit a large variety of structural and magnetic phase transitions.[9–11] Some of these compounds, for example $(C_{10}H_{21}NH_3)_2CdCl_4$, are considered as crystalline models of lipid bilayer membranes.

In this communication, we wish to report the first brief results of organic molecules intercalation into $(C_nH_{2n+1}NH_3)_2MX_4$(X: halogen) layered materials, namely 1-chloronaphthalene (hereafter $C_{10}H_7Cl$) and *o*-dichlorobenzene ($C_6H_4Cl_2$) into $(C_{10}H_{21}NH_3)_2CdCl_4$ (C_{10}–$CdCl_4$) and hexane into $(C_9H_{19}NH_3)_2PbI_4$ (C_9–PbI_4), recently obtained by us.

Experimental

A highly oriented polycrystalline film of C_{10}–$CdCl_4$ in 0.05 mm thickness was obtained by slow cooling on the surface of a hot aqueous solution, which contains $C_{10}H_{21}NH_3$ and $CdCl_2$ in the amounts of reaction stoichiometry, acidized with a few drops of aqueous HCl solution. The film was scooped onto a glass plate and dried. The film so obtained has the same c-parameter of the lattice as that already reported for a single crystal.[10] The phase transition temperatures also correspond to the reported ones.

C_9–PbI_4 single crystals were recently synthesized in our laboratory using a silica-gel technique.[12] We believe this is the first example of $(C_nH_{2n+1}NH_3)_2MX_4$ family with M=Pb and X=I. The crystal has a dark orange square-like shape of $3\times3\times0.1\ mm^3$. The details of the synthesis and complete characterization of this compound will be published elswhere soon. Here we only want to note that the C,H-chemical analysis corresponds to the assigned formula within an error of 0.05%.

By TGA it is established that in the region of 290—310 °C C_9–PbI_4 decomposes by a few steps involving melting and loses about 50% of its weight, this is in reasonable agreement with the reaction, $(C_9H_{19}NH_3)_2PbI_4 \rightarrow 2C_9H_{19}NH_3I + PbI_2$. X-Ray diffraction patterns of the remainder correspond to pure PbI_2. By optical reflectance and DSC measurements it was found that C_9–PbI_4 undergoes two phase transitions at 315 and 240 K. Under a polarizing microscope it seems that the higher temperature transition is an order-disorder one as in C_{10}–$CdCl_4$ and similar compounds. At this transition temperature the interlayer spacing changed discontinuously from 19.88 Å to 21.83 Å. The full structure determination of C_9–PbI_4 crystals is currently in progress and will be published elsewhere.

In situ X-ray analysis was carried out with the use of a Rigaku Geiger-flex Model 2027 X-ray diffractometer (with copper target). A C_9–PbI_4 single crystal of about $4\ mm^2$ or C_{10}–$CdCl_4$ film of approximately $5\ mm^2$ was mounted on a glass plate. The c-axis direction of the crystals was perpendicular to the glass surface. In the case of $C_{10}H_7Cl$, the intercalation-deintercalation process was easily observed by X-ray diffraction in the following procedure. One or two drops of $C_{10}H_7Cl$ were dropped on the C_{10}–$CdCl_4$ film and it was kept under these conditions for about 5 min. Then, excess liquid was removed by absorbing with filter paper and the glass plate was set in the diffractometer for observation. At this stage of the procedure, $C_{10}H_7Cl$ was still continuing to intercalate into C_{10}–$CdCl_4$, but that amount of $C_{10}H_7Cl$ was enough to observe all the phases of the intercalation-deintercalation process. Deintercalation proceeded after a short time of heating.

In the case of hexane and $C_6H_4Cl_2$ in situ intercalation was carried out by vapor evaporation of the liquid impregnated in cotton mounted on the back side of the glass plate. The scanning was limited only to the region of strong reflections, i.e. $2\theta=5°$—$25°$ for C_{10}–$CdCl_4$ and $2\theta=15°$—$33°$ for C_9–PbI_4. Because of the high vapor pressure of hexane, we had to use rapid scanning and a short time-constant. In spite of that, the recorded diffractograms were highly reproducible and clear. All measurements were carried out at room temperature.

Results and Discussion

1) Intercalation into C_{10}–$CdCl_4$. According to Ref. 10, C_{10}–$CdCl_4$ consists of $[CdCl_4]^{2-}$ layers sandwiched between alkylammonium chains as is shown in a simplified form in Fig. 1 (a). The ammonium end of each chain is linked to the layer by weak hydrogen bonding, N-H····Cl.

Successive changes of X-ray diffraction patterns by exposing to $C_{10}H_7Cl$ are shown in Fig. 2. As one can easily see in Fig. 2 (a), after a 5 min exposure the intensities of the host crystal diffractions decrease remarkably and a well defined series of new (001) lines appear (marked with arrows). During the intercalation process (Fig. 2 (b), (c)), the intensities of the original lines are continuously decreasing while new ones are increasing in the same manner until full intercalation is achieved (Fig. 2 (d)). During deintercalation the diffraction patterns change inversely. The diffraction patterns for the completely $C_{10}H_7Cl$ deintercalated C_{10}–$CdCl_4$ polycrystalline film is shown in Fig. 2 (f). $C_6H_4Cl_2$ intercalation-deintercalation process for

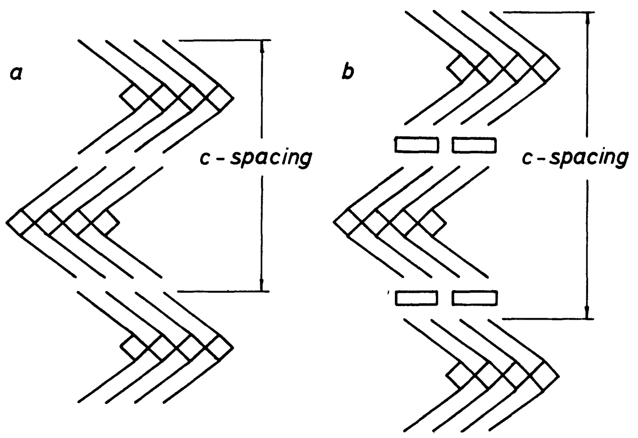

Fig. 1. Simplified schematic representation of nonintercalated (a) and intercalated (b) structures of C_{10}–$CdCl_4$.

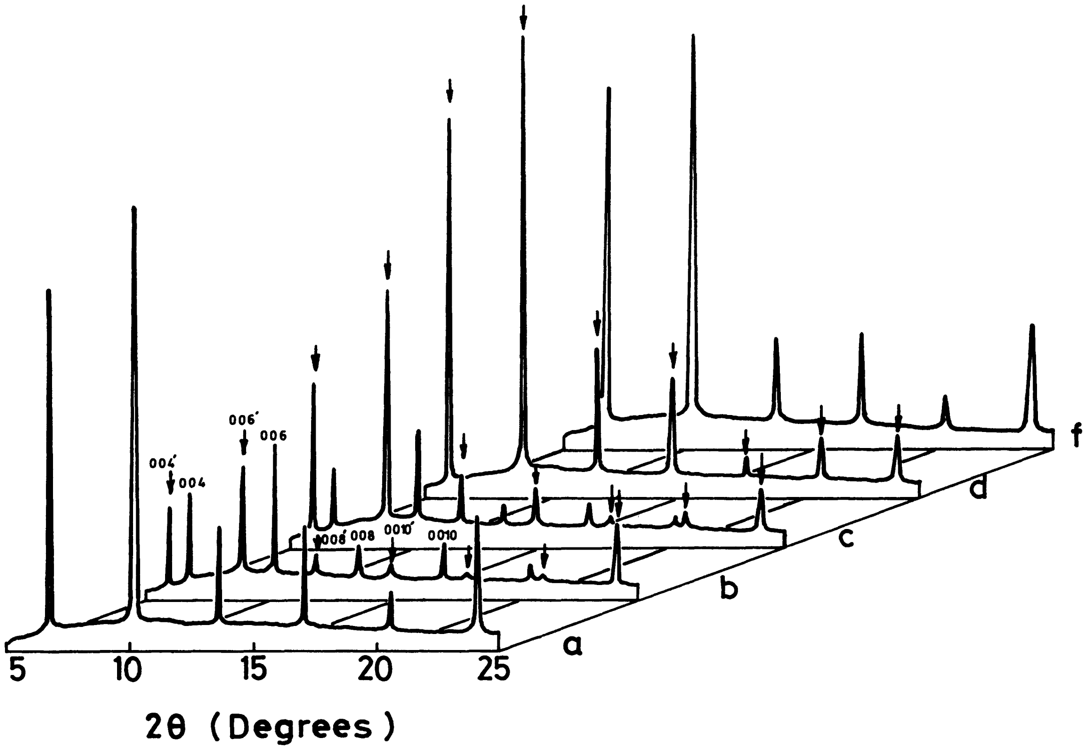

Fig. 2. X-Ray diffraction patterns of C_{10}–$CdCl_4$ during defferent phases of intercalation-deintercalation process with $C_{10}H_7Cl$. Pure C_{10}–$CdCl_4$ (a), successive phases of partially intercalated situation (b, c), fully intercalated (d), and completely deintercalated sample (f). The lines corresponding to the intercalated phases are marked with arrows. All diffraction patterns are recorded at the same sensitivity which equals to 20 kcps for the full scale.

C_{10}–$CdCl_4$ is observed in a same manner. By intercalation C_{10}–$CdCl_4$ c-spacings increased from 51.62 Å to 59.1 Å for $C_{10}H_7Cl$ and to 58.9 Å for $C_6H_4Cl_2$. In order to understand these differences and to know the exact positions of the intercalated molecules further investigations are required. The first brief results of interlayer increasing, i.e. 3.75 Å for $C_{10}H_7Cl$ and 3.65 Å for $C_6H_4Cl_2$ per one C_{10}–$CdCl_4$ layer, are in reasonable aqreement with the thickness of the aromatic rings and suggest the parallel orientation of the aromatic rings of guest molecules with the layer planes of the host crystal (Fig. 1 (b)).

The process was highly reversible. After three cycles of this procedure for the same C_{10}–$CdCl_4$ film, there was no significant change in the diffraction patterns and, surprisingly, even sharper lines were observed. For the first cycle of $C_{10}H_7Cl$ intercalation-deintercalation into C_{10}–$CdCl_4$, it took about 6 h and for the next two cycles only about 2 h. $C_6H_4Cl_2$ intercalation into C_{10}–$CdCl_4$ is remarkably faster and even for the first full cycle it required only about one hour and a half.

2) Intercalation into C_9–PbI_4. Although the full structural analysis of C_9–PbI_4 has not yet been solved, all observations of this compound suggest that C_9–PbI_4 has a similar structure to the C_{10}–$CdCl_4$ crystalline matrix in which the organic bilayers are embedded. The size of the I_6 octahedra the center of which is occupied by the Pb^{2+} ion is assumed to be the same as in PbI_2.[13)] Further we suppose that for the best orientation of the N–H····I bonding, the N-atoms of the alkylammonium chains are occupying the A sites of a perovskite-type layer and lie in approximately the same plane with unshared I atoms of I_6 octahedra similarly to C_{10}–$CdCl_4$. On these assumptions the thickness of the $[PbI_4]^{2-}$ layer is estimated to be 6.45 Å and the $C_9H_{19}NH_3^+$ chain length which is rising above and below the $[PbI_4]^{2-}$ layer is calculated to be as long as 13.33 Å, based on the same assumptions as in Ref. 14. For this arrangement and taking into account that the C_9–PbI_4 interplanar spacing is as long as 19.88 Å at room temperature, we can conclude that the direction of the alkylammonium chain is tilted about 60° with respect to the normal to the octahedra layer. The following calculations are all made on these assumptions.

In the case of C_9–PbI_4 single crystals it was easy to observe the intercalation-deintercalation process. On dropping the C_9–PbI_4 crystal into hexane the color immediately changed from dark orange to yellow, and it turned back to original color after removing the crystal from the hexane. Deintercalated crystals have a slightly deformed shape, but do not lose their integrity even after keeping for one week in hexane, and they do not lose their weight during prolonged washing on a filter with hexane.

By watching with the naked eye or a polarizing microscope it is possible to observe the introduction of such solvents as hexane, benzene, dichloromethane, dichlorobenzene, chloronaphthalene or any other soft enough solvents from the view point of intermolecular interactions. In the case of more polar and/or potentially H-bonding solvents such as tetrahydrofuran, ethanol, acetone, we observed solvation but not molecular inclusion. In the case of the introduction of $C_{10}H_7Cl$ or $C_6H_4Cl_2$, we could observe only a decrease in the intensities of the host crystal diffraction lines and disordered pattern. No lines corresponding to a new interlayer spacing appeared. Only with such a weak solvent as hexane and with fresh C_9–PbI_4 single crystals could we observe new interlayer spacings clearly and unambiguously. These results are represented in Fig. 3. The first X-ray scanning started at about 10 s after exposing the crystal to hexane vapor (Fig. 3 (b)). The

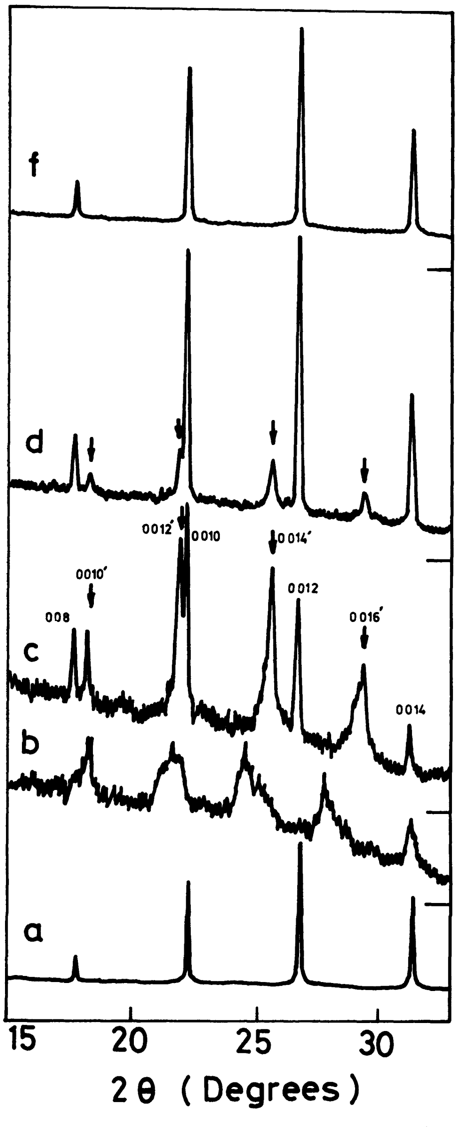

Fig. 3. X-Ray diffraction patterns of C_9–PbI_4 during different phases of hexane intercalation-deintercalation process. The lines corresponding to the intercalated phases are marked with arrows. X-Ray diffractometer full scale sensitivities correspond to 40 kcps for (a), 4 kcps for (b, c), 10 kcps for (d), and 20 kcps for (f).

diffracted patterns consist of a group of diffuse lines. We did not try to index these lines because of the nonequilibrium situation and the co-existence of multistates in this scanning. From this result we can presume only one conclusion, that the hexane intercalation into C_9–PbI_4 crystal passes through rather highly disordered states with some average interlayer spacings. On the contrary, for the next scanning (Fig. 3 (c)) the starting point was ≈5 min after the process had begun and it is clearly to be seen that these are two series of diffraction lines. One series corresponds to the host C_9–PbI_4 interlayer spacing pattern with decreased intensities, while other lines (marked with arrows) correspond to an interlayer spacing as long as 24.27 Å, or in other words a 4.36 Å increase per one C_9–PbI_4 layer. This value is reasonably close to the paraffinic chain diameter and suggests the parallel orientation of hexane chains with respect to the host crystal layers.

For the next scanning (Fig. 3 (d)), the intensities of the host crystal lines are increassing while the intensities of the new series of lines are decreasing and a completely deintercalated picture occurs after one hour (Fig. 3 (f)).

It is not impossible to observe the second cycle of hexane intercalation-deintercalation into C_9–PbI_4, but the recorded diffraction patterns become diffuse and not so clear due to the much more rapid rate of the process and a tendency to disordering.

3) General Discussion. The process we observed seems similar to the already reported results of organic molecules inclusion into paraffin layers of nickel cyanide-normal alkylamine layered systems.[15,16] However, there is a clearly distinguishable difference between these cases. In the reported case, no sharp dependence of the interlayer spacing on the amount or size of the excessively introduced amines was observed. Matsunaga clearly observed new interlayer spacings, but they did not correspond to the size of the excessively introduced molecules.[16] In our investigation all observed interlayer spacings are very clearly defined and in reasonable agreement with the size of the intercalated molecules.

As we interpret it, the main reason for such a difference between the observed processes lies in our host material structures. In their case only one layer of normal alkylamine molecules exists in between two crystalline nickel cyanide layers. Accordingly excessively introduced organic molecules penetrate inside the paraffin layer with changing of the packing coefficient of the amine molecules.[16] This pocess seems like a two-dimensional solvation with respect to the paraffin layers, or solvated intercalation with respect to the nickel cyanide layers.[17] In our cases of C_{10}–$CdCl_4$ and C_9–PbI_4 the crystals consist of organic bilayers in between two $[MX_4]^{2-}$ layers. In this case organic molecules presumably penetrate not inside but in between the alkylammonium layers retaining the full structure of C_{10}–$CdCl_4$ or C_9–PbI_4 layers perfectly unchanged. This behavior as well as reversibility are the main requirements for the exact definition of intercalation (see, for example, Ref. 17).

We believe that the existence of organic bilayers and the softness or weakness in view of intermolecular interaction forces of introduced organic molecules are the main reasons for the existence of the observed intercalation without breaking the host crystal framework structure. To our knowledge this type of introduction of molecules is reported here for the first time.

If we combine the results obtained here and reported before,[15,16] it is possible to imagine three steps of interaction processes for such layered materials and organic solvents. (i) For strong host matrixes and weak interaction guest molecules—intercalation with clearly defined new interlayer spacings corresponding to the size of the guest molecules. (ii) An intermediate situation with molecular inclusion inside paraffin layers. (iii) For weak matrixes and strong solvents–solvation leading to homogeneous solutions, for example, C_9–PbI_4 solvation in tetrahydrofuran and so on.

We belive that each member of the $(C_nH_{2n+1}NH_3)_2MX_4$ family can be intercalated with appropriate organic solvents. Moreover, we cannot exclude the possibility for similar process as secondary intercalation of long amine intercalated transition metal dichalcogenides in which an amine bilayer structure is present.

Finally, we want to note that it is difficult to imagine any charge transfer especially in the case of hexane intercalation. Thus, we believe that we really observe pure van der Waals intercalation.

We want to thank Prof. M. Sato for useful discussion. This work was done during a stay of Y. I. Dolzhenko at the Institute for Molecular Science. He would like to express his thanks to the Authorities of IMS of Okazaki National Institutes and special thanks to his host scientist Prof. Y. Maruyama for the possibility to pursue this work.

References

1) "Intercalation Chemistry," ed by M. S. Whittingham and A. J. Jacobson, Academic Press (1982).

2) F. R. Gamble, J. H. Osieck, M. Cais, R. Pisharody, F. J. Disalvo, and T. M. Geballe, *Science*, **174**, 493 (1971).

3) M. S. Whittingham, *Progr. Solid State Chem.*, **12**, 41 (1978).

4) L. B. Ebert, *J. Mol. Catalysis*, **15**, 275 (1982).

5) V. M. Koshkin, *Latv. PSR Zinat. Akad. Vestis, Fiz. Teh. Zinat. Ser.*, **1981**, 90.

6) A. M. Ghoryeb, C. C. Coleman, and A. S. Yoffe, *J. Phys. C. Solid State Phys.*, **17**, L715 (1984).

7) A. P. Mil'ner, Yu. R. Zabrodskii, V. M. Koshkin, V. V. Kukol, E. B. Yagubskii, and G. D. Guseinov, *Zh. Strukt. Khim.*, **21**, 93 (1980).

8) Y. Maruyama, unpublished result.

9) R. Kind, *Ber. Bunsenges. Phys. Chem.*, **87**, 248 (1983).

10) R. Kind, S. Plesuko, H. Arend, R. Blinc, B. Zeks, J. Selinger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajar, F. Milia, and G. Chapuis, *J. Chem. Phys.*, **71**, 2118 (1979).

11) J. Etxebarria, J. Fernandez, M. A. Arriandiaga, and M. J. Tello, *J. Phys. C; Solid State Phys.*, **18**, L13 (1985).

12) E. A. Ziger, "Rost i svoistva kristallov," Kharkov (1980), p. 8.

13) R. W. G. Wyckoff, "Crystal Structure," John Wiley, New York (1963), Vol. 1, p. 269.

14) Ref. 1, p. 239.

15) Y. Mathey, R. Setton, and C. Mazieres, *Can. J. Chem.*, **55**, 17 (1976).

16) K. Takayanagi and Y. Matsunaga, *Nippon Kagaku Kaishi*, **1983**, 277.

17) Ref. 1, p. 315.