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Preparation of a Layered Double Hydroxide-Porphyrin Intercalation Compound

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5,10,15,20-tetra(4-sulfonatophenyl)porphin (TSPP) is intercalated into the interlayer space of hydrotalcite by anion exchange. The intercalated porphyrin anions are possibly arranged with the molecular plane perpendicular to the hydroxide layers.

Hydrotalcite (HT), $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2}\cdot H_2O$ ($0.2<x\leq0.33$), is a layered double hydroxide with exchangeable interlayer anions. Since there have already been several reports on organic intercalation into HT, various host-guest interactions can be expected in the interlayer regions. Therefore, HT is one of the good candidates for the production of inorganic-organic composite materials at molecular level.

Recently, tetrasodium TSPP (Na_4TSPP) has been found to show a high temperature photochemical hole burning (PHB) above liquid N_2 temperature using polyvinylalcohol as the matrix.1) The interactions between PHB materials and various host substances are very interesting from the viewpoint of the development of novel PHB materials. With regard to the intercalation of porphyrins into inorganic layered materials, only the smectite group of clay minerals has been known to take up several cationic porphyrins.2,3) However, there have been no attempts to obtain the intercalation compounds from HT which shows an anion exchange property. Therefore, in the present study, the intercalation of TSPP into HT has been attempted.

Na_4TSPP (Wako Pure Chem. Ind.) was used without further purification. HT-Cl was prepared by hydrolysis of a $AlCl_3\cdot 6H_2O$ and $MgCl_2\cdot 6H_2O$ mixed solution with a NaOH solution.4) All of the procedures were performed with decarboxylated water and under a nitrogen atmosphere to minimize the effect of carbonate anions. Anion exchange capacity (A.E.C.) of the product was 2.8 meq/g, which was 85% of the theoretical value based on the Al contents. This fact indicated the presence of a small amount of carbonate anions in HT-Cl. Na_4TSPP (0.62 g; 5×10^{-4} mol) was dissolved in water (0.1 dm^3) and HT-Cl (0.14 g) was added into the solution. After the suspension was stirred at 60 °C for a week, the reaction product was washed, and dried in reduced pressure at room temperature.

A HT-TSPP intercalation compound was formed by anion exchange. The X-ray powder diffraction patterns of HT-Cl and HT-TSPP are shown in Fig. 1. The basal spacing of the HT-TSPP increased to 22.4 Å from 8.0 Å of HT-Cl. The gallery height of HT-TSPP was 17.6 Å when the thickness of brucite layers (4.78 Å) was subtracted. This increase in the gallery height strongly indicated the intercalation of the porphyrin. The CO_3-exchanged HT (d_{003}= 7.8 Å) was also detected in the X-ray diffractogram.

The IR spectrum of the HT-TSPP also showed the characteristic bands due to TSPP. The sulfonate bands of the product appeared at 1220, 1187, 1124, and 1037 cm^{-1}. Compared with the Na_4TSPP,5) the bands of the product slightly shifted to lower frequency regions. The organic content in the product was H: 4.00%, C: 19.6%, N: 2.06%, indicating that 81% of Cl^- ions was replaced with $TSPP^{4-}$ ions (1.47 meq/g). Since the CO_3^{2-} content increased further in the reaction product, the amount of TSPP to the A.E.C. was not correctly determined. However, the separation of the XRD peaks due to HT-TSPP and HT-CO_3 suggested that the TSPP content in the interlayers of the HT-TSPP was fairly high.

In the ^{27}Al-MASNMR spectra, the chemical shift of Al in the HT-TSPP as well as in the HT-Cl was 9.5 ppm, which indicated that octahedrally coordinated Al atoms in the hydroxide layers were not influenced by the reaction. The visible absorption spectrum of the HT-TSPP was similar to that of the Na_4TSPP in solid, although the Soret (B) bands in solid were very weak and different from that of an aqueous Na_4TSPP solution.6) This fact suggested that TSPP anions were closely packed in the interlayer spaces.

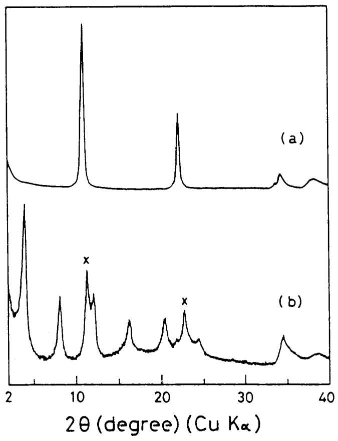

Fig.1. XRD patterns of (a) HT-Cl and (b) HT-TSPP intercalation compound. X: HT-CO_3.

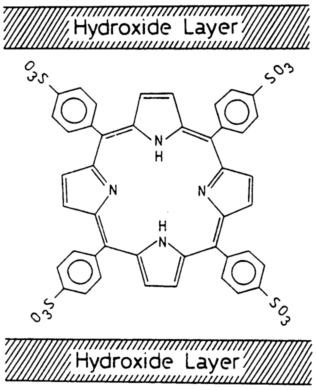

Fig.2. Postulated configuration of intercalated TSPP anion in the interlayer space.

In conclusion, TSPP anions were intercalated in the interlayers of HT. Based on the data of bond lengths for tetraphenylporphyrin,7) the size of TSPP molecular plane was estimated to be ca. 18 Å x 18 Å. From these results on the gallery height, the layer charge density of HT, the TSPP content, and the size of the TSPP anion, it was suggested that the intercalated porphyrin anions were possibly arranged with the molecular plane perpendicular to the hydroxide layers. The postulated configuration in the interlayers is shown in Fig.2.

References 1) K. Sakoda, K. Kominami, and M. Iwamoto, Jpn. J. Appl. Phys., 27, L1304 (1988). 2) S.S. Cady and T.J. Pinnavaia, Inorg. Chem., 17, 1501 (1978). 3) H. Kameyama, H. Suzuki, and A. Amano, Chem. Lett., 1988, 1117. 4) S. Miyata, Clays & Clay Miner., 23, 369 (1975). 5) T.S. Srivastava and M. Tsutsui, J. Org. Chem., 38, 2103 (1973). 6) V. Skarda and M.M. Labes, Mol. Cryst. Liq. Cryst., 126, 187 (1985). 7) S.J. Silvers and A. Tulinsky, J. Am. Chem. Soc., 89, 3331 (1967).

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