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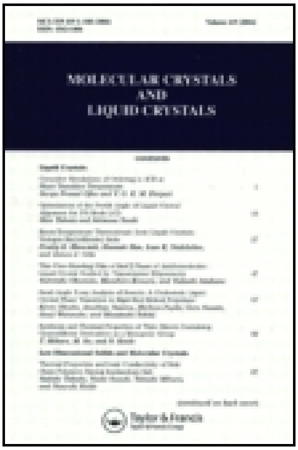

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Synthesis and Characterization of Intercalated Layered Double Metal Hydroxides With Interlayer Aromatic Molecular Anions: Intercalation of 9,10-Anthraquinonedisulfonates Between Layers of Mg and Al Layered Double Hydroxides(MgAl-LDH)

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SYNTHESIS AND CHARACTERIZATION OF INTERCALATED LAYERED DOUBLE METAL HYDROXIDES WITH INTERLAYER AROMATIC MOLECULAR ANIONS:
INTERCALATION OF 9,10-ANTHRAQUINONEDISULFONATES BETWEEN LAYERS OF Mg AND Al LAYERED DOUBLE HYDROXIDES(MgAl-LDH)

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Abstract 9,10-Anthraquinonedisulfonates (AQij; ij=15, 18, 26 and 27) are intercalated between layers of synthetic hydrotalcite. Two or three values of enhanced interlayer distance are observed in powder X-ray diffraction (XRD) patterns of separate solid samples when AQ26 or AQ27 is intercalated, respectively. Dimensions are compared between the distance and the guest molecular size which is estimated in a semiempirical MO calculation. This multiplicity is elucidated as a result of distinct molecular orientations of the interlayer AQij dianion which bridges between adjacent layers of Mg/Al-LDH. The solid state chemistry of the AQij-intercalated products is described on the basis of elemental analysis, diffuse reflection (DR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

INTRODUCTION

Synthetic hydrotalcites (HT) have positively charged layers of Mg/Al-LDH and negatively charged interlayers with the formula $[Mg_xAl_y(OH)_{2(x+y)}][A_zB_{(y-z)/2}\cdot nH_2O]$ (A and B at the interlayer gallery are mono- and di-valent anions, respectively) showing basal spacing d=7.6-7.8Å in XRD patterns when both A and B are small inorganic anions.[1-3] These interlayer anions balances excess charge of the layer which charge originates from the isomorphous replacement from Mg^{2+} to Al^{3+}. A new category of composites appears, which has an architecture including both inorganic host and organic guest components in a microscopic nanometer scale. It has been displayed that the orientation of the interlayer aromatic dianion governs the dimension of the interlayer distance in the systems of naphthalenedisulfonates-Zn/Al-LDH[4] and AQ26-Mg/Al-LDH.[5]

In this work, the intercalation of four isomers of 9,10-anthraquinonedisulfonate between layers of Mg/Al-LDH in synthetic HT is described. Multiplicity in the enhanced interlayer distance of the AQ26- and AQ27-intercalated products is elucidated as a result of distinct size of the guest along the *c*-axis of the microcrystals.

EXPERIMENTAL

Syntheses and analyses of the AQ26-intercalated Mg/Al-LDH has been described.[5] AQ15-, AQ18- or AQ27-intercalated Mg/Al-LDH was obtained similarly. Ordinal C H elemental analysis of these solid samples was done. By chelatometric titration, metal components were quantitatively determined.[6] Chloride content was less than 0.1% of the total sample mass commonly in all intercalated products thus it is omitted from the formulae in TABLE 1as well as water content.

XRD, XPS and DR spectroscopic measurements and MO calculation were carried out as described before.[4, 7] Under the reduced pressure (10^{-5}-10^{-6} Pa), a Mg cathode ($h\nu$=1253.6 eV; 10 kV/30 mA) was used in XPS. A semi-empirical MO calculation was carried out with the MOPAC/PM3 program[8] with a set of initial parameters in molecular geometry previously reported.[9] The molecular structure was discussed[4] which gave the lowest value of the formation enthalpy (ΔH_f) in the optimization with respect to bond lengths, bond angles and dihedral bond angles.

RESULTS AND DISCUSSION

Owing to the intercalation of AQ27 between the layers of Mg/Al-LDH, the basal spacing in XRD patterns is enhanced from d=7.715Å (2θ=11.46°) to *ca.* 19Å (19Å phase), to *ca.* 15Å (15Å phase) or to *ca.* 12Å (12Å phase). It has been reported that the unit cell of HT has hexagonal symmetry with a lattice constant a_0=0.306 nm and with the c axis perpendicular to the layers.[1,2] Indexing the patterns are also listed in FIGURE 1 with the assumption that the unit cell symmetry and the a_0 dimension was the same as those of HT but that the dimension of the other lattice constant c_0 differs among the products. The symmetric and sharp basal (001) diffraction is associated with a sequence of

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prominent (00*l*) lines in all the patterns and shows that all the phases are pure products. This observation indicates that the brucite-like layers (4.769Å in thickness[2]) in the intercalated products have the well developed stacking in the direction parallel to the *c*-axis.[1] Basal spacings of all the phases are listed together with the other results in TABLE 1 which will be discussed later. Two values in the basal spacing are also observed when AQ26 is intercalated instead of AQ27, although only the 12Å phase has been obtained so far under the hydrothermal condition at 127±1°C in aging precipitates. Only a single phase has been observed when AQ15 or AQ18 is intercalated. The position of two $-SO_3^-$ groups in the interlayer AQij thus apparently governs both the selection whether the multiplicity in basal spacing appears or not and the degree of the multiplicity. Although the mechanism is not known, it is interesting that the multiplicity appears preferably with isomers having two $-SO_3^-$ groups at the most distant positions from the carbonyl groups in anthraquinone.

Except for a gradual signal rise to the short wavelength side, the guest AQij molecule is responsible for all the absorption maxima in the DR spectra of AQij-intercalated products. An absorption appears at around λ=315nm due to the $^1B_{2u}(\pi,\pi^*)\leftarrow S_0$ transition of anthraquinone.[10] Considering that no significant change is noticed when the spectra are compared with each other among all the AQij-intercalated products, it is concluded that the interlayer AQij molecules commonly hold the planar framework of the conjugated π-electron system in the anthraquinone moiety. A weak absorption due to the $^1B_{1g}(n,\pi^*)\leftarrow S_0$ transition to the lowest singlet state of anthraquinone[10] is located at around λ=485nm in the DR spectrum of the solid sodium salt of AQij. Instead of this band location, a broad absorption appears at λ_{max}=501-526nm. Negative check confirms that this absorption is due to the intercalation of AQij. Judging from the comparable intensity of this band to the allowed $(\pi,\pi^*)\leftarrow S_0$ transition described above, it is concluded that this is a new kind of absorption which originates from electronic interaction(s) between the conjugated π-electron system in the guest molecule and other orbital(s) in the intercalated product. The definite assignment of this band is now under investigation.

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XPS wide scan spectra of the AQij-intercalated products commonly show several peaks which are assigned to core level electrons emitted from C, S, O, Al and Mg.[11] The binding energy of Al 2p electron is 74.0±0.9 eV and 73.7±0.9eV for the 19Å and the 12Å phases, respectively; the variation of the energy due to the difference in the basal spacing is insignificant. These value agrees with that of the octahedrally coordinated Al^{3+} within experimental errors.[12] Since the HT without AQij has 73.6eV,[4] it is concluded that no significant change takes place in the chemical status of this cation in the layers upon the intercalation of AQij. A very weak signal at around 200eV is observed in a few samples after they are etched by Ar^{+} bombardment for 60s. It corresponds to tiny quantity of Cl^{-} detected by the potentiometric titration previously described.

Typical results of the AQij-intercalated products are listed in TABLE 1 including basal spacings and chemical compositions. Since each of these phases has *never* been produced as a mixture, it is concluded that the optimum synthetic condition for each phase is not overlapped. Although the 12Å phase in the AQ26-intercalated product is preferable in the hydrothermal condition as previously described, both two phases and all of three phases in AQ27-intercalated products are thermodynamically stable at room temperature because no mutual transformation is observed in XRD patterns after the solid samples are left in air for a month. The XRD, XPS and DR spectroscopic results force us to conclude that the multiplicity in the basal spacing is originated from the distinct dimension of interlayer distance which is governed by the size of the interlayer guest AQij molecules along the *c*-axis.

The Al/(Al+Mg) ratio in TABLE 1 remains within limits for HT reported previously.[2] The interlayer distance of the 19Å phase of the AQ26-intercalated product is 14.26Å which is just less than the calculated guest molecular size l_M=15.285Å in TABLE 1. This is rationalized if we assume that an orientation of the interlayer AQ26 molecule bridging as a bidentate between adjacent layers of Mg/Al-LDH, which has been proposed in the cases of 26NDS between layers of Zn/Al-LDH, ClO_4^- and SO_4^{2-} both between layers of Mg/Al-LDH.[2,4,5,13] This orientation is held by the attraction between the positive charge on Al^{3+} in the layer and the negative one on $-SO_3^-$ in the AQ26 anion at the interlayer. A slightly tilted molecular plane of the interlayer AQ26 relative to the inner

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surface of the layer is suggested for the 19Å phase and a more tilted one is supposed for the 12Å phase. A similar orientations are proposed for interlayer AQ27 anions in three phases of intercalated products.

This bridging model of the guest anions leads to the upper limit of the AQ26/Al ratio is 0.5. The ratio in the analysis is lower than this limit since the intercalation of CO_3^{2-} is not negligible as is indicated in the analytical formulae in TABLE 1. In the 19Å phase, the ratio are larger than that in the 12Å phase. A reason is that the orientation of the interlayer AQ26 anions in the former phase is such that they take the close-packed structure thereby a high ratio is realized whereas the anions in the latter phase do not take the structure. Steric hindrance due to the bulky anthraquinone moiety is supposed for the reason of it although no reason is supposed for the AQ27-intercalated products.

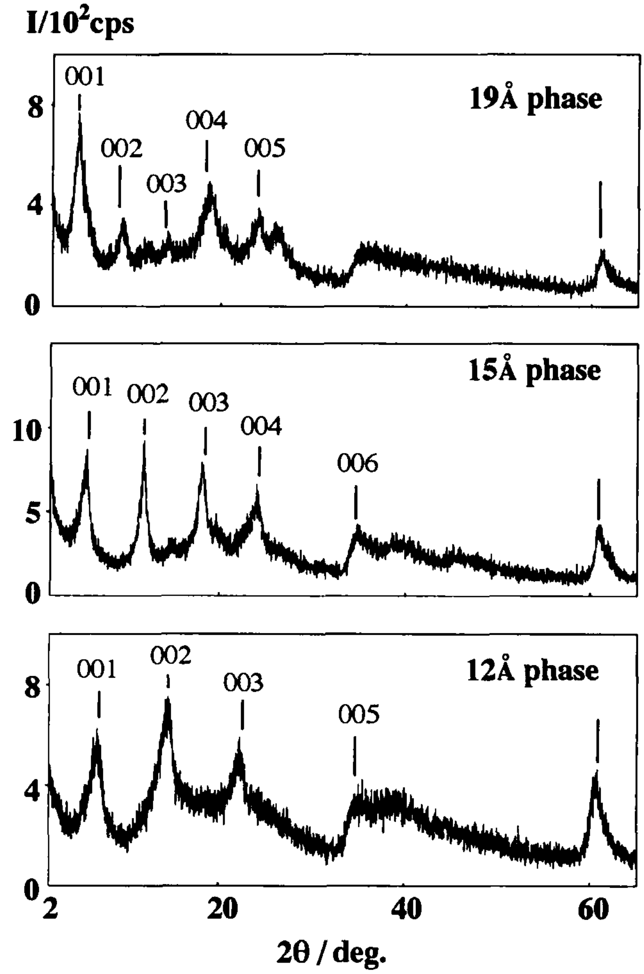

FIGURE 1 Indexing in XRD patters of intercalated Mg/Al-LDH with interlayer AQ27 by means of the Ni-filtered CuKα_1 line (λ=1.54050 Å); the19Å phase (upper) with diffraction lines at 2θ= 4.780° (001), 9.500° (002), 14.20° (003), 18.82° (004), 24.10° (005) and 61.28° (110); the 15Å phase (middle) with lines at 5.880° (001), 11.94° (002), 17.84° (003), 24.14° (004), 34.82° (006) and 60.70° (110); the 12Å phase (lower) with lines at 2θ=7.220°(001), 14.34° (002), 22.18° (003), 35.60° (005) and 60.82° (110).

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TABLE 1 Summary of experimental results AQij-intercalated products

AQij	E1)/eV	l_M2)/Å	*d*3)/Å	COMPOSITIONS	notes
AQ15	74.0±0.9	12.882	11.64	$MgAl_{0.31}(OH)_{2.93}(CO_3)_{0.06}(AQ15)_{0.09}$	-
AQ18	73.8±0.8	10.444	11.46	$MgAl_{0.43}(OH)_{2.85}(AQ18)_{0.21}$	-
AQ26	73.9±0.9	15.285	12.73	$MgAl_{0.47}(OH)_{2.94}(CO_3)_{0.12}(AQ26)_{0.12}$	12Å phase
			19.03	$MgAl_{0.47}(OH)_{2.95}(CO_3)_{0.04}(AQ26)_{0.19}$	19Å phase
AQ27	73.8±0.9	15.520	12.23	$MgAl_{0.22}(OH)_{2.39}(AQ27)_{0.13}$	12Å phase
			15.02	$MgAl_{0.33}(OH)_{2.63}(AQ27)_{0.19}$	15Å phase
			18.47	-	19Å phase

1)binding energy of Al 2p electron in XPS. 2)molecular size: the sum of ionic diameter of anionic oxygen (2.56Å) and the interatomic distance between two anionic oxygens in different $-SO_3^-$ groups in AQij whose geometry is optimized by MO calculation, see text. 3)interplanar spacing obtained d(00*l*) in XRD patterns.

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