Incorporation of Phthalocyanines by Cationic and Anionic Clays via Ion Exchange and Direct Synthesis

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Phthalocyanines (Pc) and metallophthalocyanines were incorporated into the galleries of anionic and cationic clays via ion exchange and in situ crystallization of the synthetic clay layers. Intercalation compounds between the layered magnesium silicate clay hectorite and cationic phthalocyanines were directly prepared by refluxing for 2 days aqueous solutions of silica sol, magnesium hydroxide, lithium fluoride, and either alcian blue dyes (Cu(II)Pc) or 15-crown-5 tetra-substituted phthalocyanine (15C5Pc). The CuPc dyes are tetrapositively charged through peripheral quaternary ammonium groups, whereas the 15C5Pc is electrically neutral. Anionic clays prepared by hydrolysis of mixed solutions of aluminum nitrate, magnesium nitrate, and copper(II) phthalocyaninetetrasulfonic acid, tetrasodium salt (CuPcTs) in sodium hydroxide resulted in crystallization of an intercalation compound between a layered double hydroxide (LDH) and this anionic Pc. The material prepared by ion exchange of CuPcTs into a wet, freshly prepared LDH was superior in crystallinity. The phthalocyanines are oriented parallel to cationic hectorite clay layers (gallery heights 4.5–6.5 Å) and perpendicular to anionic layered double hydroxide clay layers (gallery height 18.2 Å) in correlation with their hosts' respective layer charge densities.

Introduction

Smectite clay minerals and layered double hydroxides (LDHs) are materials composed of charged layers that can be classified into two groups, termed cationic and anionic clays, respectively, depending upon the charge of the compensating ion within the interlayer or gallery region. The intracrystalline reactivity of layered compounds is reflected in their ability to bind guest molecules between the layers via mechanisms such as solvation, ion exchange, complexation, and swelling.[1] A unique aspect of layered double hydroxides is that they are the only intracrystalline-reactive layered compounds composed of positively charged layers.[1] The ion-exchange chemistry of both cationic and anionic clays is well-established, including the exchange of organic complexes. Relatively few studies, however, have concentrated on the method of direct synthesis, despite the possibility of preparing novel intercalation compounds not accessible by ion exchange. Recently, water-soluble porphyrins and metalloporphyrins were successfully investigated as flat macrocycles to induce the crystallization of hectorite clay layers in a "pseudotemplate" fashion.[2] A few reports of using direct synthesis to incorporate organic anions into layered double hydroxides include terephthalate[3] and long-chain carboxylic acids,[4] although the latter study first heated the LDH to 500 °C to convert it to the oxide form and then reconstituted the LDH in the presence of glycerol.

Previous reports of intracrystalline reactions of dye molecules in layered double hydroxides concern the anion

exchange of naphthol yellow S[5] and indigo carmine and new coccine.[6] The latter study by Park et al.[6] also constitutes the only prior report thus far claiming the direct synthesis of organic dyes into layered double hydroxides. Several papers have appeared involving the synthesis of smectite clay–dye compounds via ion exchange and their significant spectral properties.[7] Organic dye molecules as interlayer guest species are intriguing because their host–guest interaction may impart unique structural features and physicochemical properties.

A systematic study of the use of phthalocyanine (Pc) dye molecules during direct synthesis and ion exchange of both cationic and anionic clays has now been carried out. Molecules based on a copper(II) phthalocyanine (CuPc) system were selected for both anionic and cationic types of clays (see Figure 1). Derivatization of the Pc system by charged substituents is straightforward and can be tailored to the application; that is, cationic CuPc alcian blue dyes and anionic CuPc tetrasulfonate (CuPcTs) compensate the charge of cationic smectite clays and anionic LDHs, respectively. It was also of interest to probe the potential of a complex, neutral molecule like 15-crown-5 tetrasubstituted Pc (15C5Pc) as a "template" in clay synthesis. Macrocyclic compounds such as crown ethers and cryptands can be intercalated in homoionic smectites, yielding stable intracrystalline polydentate coordination complexes[8,9] that have been extensively studied by IR, XRD, UV–visible spectroscopy, and laser microprobe

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Incorporation of Phthalocyanines by Clays

Chem. Mater., Vol. 5, No. 4, 1993 473

Figure 1. Structures of phthalocyanines used in this study. AB is a dye called alcian blue; two different variants are shown. CuPcTs is copper(II) phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid, tetrasodium salt, and 15-crown-5 Pc (15C5Pc) is [[4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyanine].

MS.[10] All ion-exchanged and synthetic materials were compared using X-ray powder diffraction, surface area measurements, and microanalysis.

Experimental Section

Materials. All inorganic starting materials were of reagent grade quality. Ludox silica sol HS-30, a Na$^+$-stabilized 30 wt % aqueous solution of average particle size 12 nm, was obtained from DuPont. Dye molecules were purchased from Aldrich, including alcian blue 8GX (AB) (certified dye, ingrain blue 1, dye content 88%), alcian blue pyridine variant (AB, pyr; dye content ≈ 90%), and copper(II) phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid, tetrasodium salt (CuPcTs, dye content ≈ 85%). 15-Crown-5 Pc (15C5Pc, 4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,-13-pentaoxatridecamethylene)phthalocyanine] was prepared using a combination of two previously reported methods.[11,12] All water used was both distilled and deionized. Structures of all these phthalocyanines are presented in Figure 1.

Synthesis of 15C5Pc. First, dibromobenzo-15-crown-5 (DBB-15C5) was prepared in the following manner: 10 mL of dry methylene chloride containing 0.121 mol of bromine was added dropwise over 1.5 h at 0 °C to a stirring mixture of 0.0564 mol of benzo-15C5, 0.401 g of iron powder, and a large crystal of iodine in 150 mL of dry methylene chloride. This mixture stirred at room temperature for an additional 18.5 h and then was filtered and poured into 150 mL of 10% aqueous NaOH. After filtering, the organic layer was separated, washed with water, and dried (anhydrous MgSO$_4$). The dry organic layer was evaporated to give orange crystals which upon recrystallization from 50 mL of ethanol gave 62.0% yield of DBB-15C5 (colorless crystals). This was then used to prepare dicyanobenzo-15-crown-5 (DCB-15C5).

A mixture of 0.0376 mol of DBB-15C5 and 0.113 mol of CuCN in 150 mL of dimethylformamide (DMF was distilled from BaO under vacuum) was brought to reflux with stirring for 5 h under dry nitrogen. Upon cooling, 300 mL of concentrated aqueous NH$_3$ was poured into the reaction mixture and air was bubbled through for 17 h. The mixture was filtered through a layer of celite sitting over a thin layer of sand on filter paper in a Büchner funnel. The green solid material was washed with 10% NH$_4$OH and then water until the filtrate was pH neutral. The green solid (along with celite and sand) was dried overnight in a vacuum oven at 60 °C and Soxhlet-extracted with toluene for 4 days. The toluene extracts were concentrated to give yellow crystals which upon recrystallization from benzene gave 52.3% yield of DCB-15C5 (colorless crystals).

15C5Pc was made by first stirring a solution of 0.0195 mol of DCB-15C5 in 25 mL of N,N-dimethylaminoethanol at reflux for 19 h while NH$_3$ gas was bubbled through. The mixture upon cooling was dissolved in 650 mL of 2:1:1 chloroform:methylene chloride:ethanol and added slowly dropwise to 1600 mL of stirring ethyl acetate. The green precipitate was allowed to settle and then collected. The reprecipitation was repeated and the product dried overnight in a vacuum oven at 60 °C to yield 2.8g (45.0%). IR (KBr), cm^{-1}: 3300 (N–H), 1610 (Ar ring), 1203–1281 (C$_{Ar}$–O–C), 1050–1130 (C–O–C), 1027 (N–H); UV–vis: 700, 662, 644, 600 nm. FAB-MS: m = 1275, calcd MW 1273. Microanalysis: 56.7% C, 5.7% H, 8.3% N (C/N = 8.0); calcd 60.3% C, 5.85% H, 8.8% N (C/N = 8).

Direct Synthesis of Pc–Hectorite Intercalation Compounds. Synthetic hectorites were prepared as described previously.[2] The structural composition of an ideal hectorite clay[13] is [Li$_{0.66}$Mg$_{5.34}$Si$_8$O$_{20}$(OH)$_4$](Ex^{n+})$_{0.66/n}$ where Li(I) substitutes for Mg(II) in the octahedral layer, Si(IV) is in the tetrahedral layer, and Ex is an exchangeable cation. Aqueous gels consisting of 0.06:0.20:1.00:1.52 organic complex:LiF:MgO:SiO$_2$ molar ratios were refluxed for 2 days, then centrifuged, washed until the decant was clear, and air-dried. Only freshly prepared Mg(OH)$_2$ sols were used as the source of MgO, which were thoroughly washed after precipitation from MgCl$_2$ in dilute NH$_4$OH. The water solubility of the alcian blue dyes was very high, while that for 15C5Pc was acceptable only upon sonication of a water slurry of this Pc for a few minutes prior to use in the clay precursor gel. Samples prepared in this fashion are denoted as, for example, synthetic AB–hectorite.

Direct Synthesis of Pc–LDH Intercalation Compounds. Layered double hydroxides (LDHs) are minerals based on the hydrotalcite structure, for which the structure is expressed by the formula [Mg$_{1-x}$Al$_x$(OH)$_2$(A^{n-})$_{x/n}$·mH$_2$O, where 0.2 < x ≤ 0.33 and A is the interlayer anion.[5] Direct synthesis was carried out by hydrolysis of mixed aqueous salt solutions in the presence of sodium hydroxide.[6] Specifically, three separate solutions of mixed magnesium nitrate (0.075 M) and aluminum nitrate (0.025 M), 0.0125 M CuPcTs, and 0.20 M NaOH were simultaneously and slowly added dropwise with stirring to water (previously adjusted to pH 10.5 with NaOH) in a three-neck round-bottom flask under a nitrogen atmosphere. A nitrogen purge is necessary to suppress the strong affinity that LDH compounds have toward binding carbonate anions (from the air). After equal volumes of each solution had been dispensed into the slurry, the suspension was left to stir overnight at 65 °C under nitrogen. The product was then filtered, washed extensively with water, and air-dried. This sample is referred to as synthetic CuPcTs-LDH. Note that the concentration of CuPcTs used is twice that necessary to balance the charge created by aluminum substitution in the LDH framework. Using the correct stoichiometry a mixture of products as determined by XRD was found, with the major component Mg-Al-CO$_3$ LDH.

Ion-Exchanged Compounds. For cation exchanges, the natural clay mineral hectorite SHCa-1 was used. As received from the Source Clays Repository, Columbia, MO, this Na$^+$-hectorite contains nearly 50% by weight calcium carbonate impurity. This was removed prior to use, along with some iron, by conventional sedimentation techniques. Using X-ray powder

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474 *Chem. Mater., Vol. 5, No. 4, 1993*

Carrado et al.

Table I. Physical Properties of Synthetic and Ion-Exchanged Phthalocyanine-Containing Clays

clay	XRD	%C	%N	C/N theor	C/N expt	SA,[a] m²/g	org iec,[b] mequiv/100 g
cationic	d(001), Å						
SHCa-1[c]	15.2					71	(80)[d]
dil AB–SHCa	14.3	4.46	0.94	4.7	5.5	64	23
conc AB–SHCa	14.1	20.8	4.98	4.7	4.9	<5	90
syn AB–hectorite	14.0	8.19	2.36	4.7	4.1	206	36
dil AB,pyr–SHCa	14.3	3.85	1.01	5	4.4	65	20
conc AB,pyr–SCHa	15.7	21.1	4.59	5	5.4	3	110
syn AB,pyr–hectorite	15.7	5.77	1.49	5	4.5	167	31
dil 15C5Pc–SHCa	16.6	13.7	2.03	8	7.9	<5	18[e]
conc 15C5Pc–SHCa	18.6	26.2	3.70	8	8.3	<5	34[e]
syn 15C5Pc–hectorite	16.0	5.30	0.74	8	8.3	213	7[e]
anionic	d(003), Å						
LDH	8.20					2.5	(218)[d]
CuPcTs–LDH	23.0	17.2	5.20	4	3.9	1.1	179
syn CuPcTs–LDH	22.5	20.5	5.65	4	4.2	0.2	214

[a] N_2 BET surface areas. [b] Ion-exchange capacity of organic based on %C content. [c] SHCa = purified natural hectorite. [d] These are literature values for total ion exchange capacity. [e] Units are mmol/100 g (not mequiv) because charge is not known. syn = synthetic; dil = dilute; conc = concentrated; AB = alcian blue 8GX; AB, pyr = alcian blue, pyridine variant; 15C5Pc = tetrakis(15-crown-5) phthalocyanine; CuPcTs = copper(II) phthalocyaninetetrasulfonate; LDH = Mg–Al–NO₃ layered double hydroxide.

diffraction, an estimate of <2% $CaCO_3$ remains in the slurry after this separation. Two different concentrations of each dye were used in order to form clays with differing levels of dye incorporation. Ion-exchange salts were added to the clay slurry to a final concentration of 0.14–0.84 mM, then stirred for 18–24 h at room temperature, centrifuged, washed until decants were clear, and air-dried. These samples are referred to as the "dilute" ion-exchanged compounds. A range of 2.5–5.0 mM dye resulted in "concentrated" samples. Ion-exchange of 15C5Pc took place at 60 °C for 2 days. Thin films were prepared by air-drying a small portion of the slurry on a glass microscope slide. Ion-exchanged samples are abbreviated, for example, as dilute AB-SHCa.

A Mg–Al–NO₃ LDH slurry for ion-exchange was prepared in the following manner. Solutions of mixed magnesium nitrate (0.075 M) and aluminum nitrate (0.025 M) and 0.20 M NaOH were added simultaneously and slowly dropwise with stirring to water (previously adjusted to pH 10.5 with NaOH) in a three-neck round-bottom flask under a nitrogen atmosphere. After equal volumes of each solution had been dispensed into the slurry, the suspension was left to stir overnight. Then 200 mL of the LDH slurry were placed in a dropping funnel fitted in one neck of a three-neck 1-L round-bottom flask containing 100 mL of a 0.005 M CuPcTs solution in DDW and purged with nitrogen. After the LDH slurry was slowly added at 40 °C, 200 mL more of the CuPcTs solution was added via the same method, followed by a remaining 400 mL of LDH. The product was then stirred and aged at 70 °C for 2 days, then filtered, washed with DDW, and air-dried. This ion-exchanged sample is referred to as CuPcTs-LDH. Pure Mg–Al–NO₃ LDH was prepared by dropwise addition of 0.20 M NaOH and a mixed solution of 0.025 M aluminum nitrate and 0.075 M magnesium nitrate to water adjusted to pH 10.5 (with the 0.20 M NaOH) under a nitrogen atmosphere. The slurry was allowed to stir for an additional 72 h at 65 °C, then filtered, washed, and air-dried. Simply redispersing a dry LDH in water and adding a CuPcTs solution for ion-exchange, even at elevated temperatures, did not result in satisfactory products.

Characterization. X-ray powder diffraction (XRD) experiments were carried out on a Scintag PAD-V instrument using Cu Kα radiation at a scan rate of 0.5° 2θ/min. The instrument was calibrated to the (101) reflection of low-quartz at 3.34 Å. Samples were run as the oriented films prepared on glass slides or as powders in horizontally held trays. Microanalysis determinations were performed either by Commercial Testing & Engineering, S. Holland, IL, or by the ACL division of Argonne National Lab. Nitrogen BET surface areas were determined on a Quantasorb sorption analyzer from Quantachrome Corp. Samples were fully outgassed for 18–48 h under nitrogen prior to measurement: SHCa was heated at 150 °C, other hectorites were heated at 100 °C, and LDHs were heated at 130 °C. Correlations of fits to the BET data were in the range 0.99–1.00.
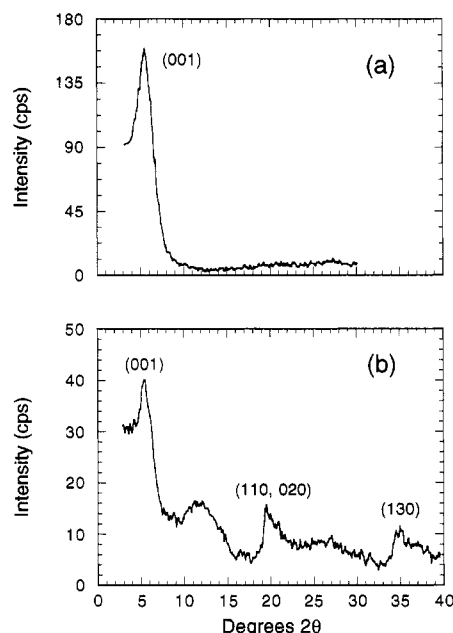

Figure 2. X-ray powder patterns of (a) a thin film of synthetic alcian blue, pyridine variant–hectorite and (b) a powder pattern of synthetic 15-crown-5 phthalocyanine–hectorite; (hkl) reflections are indicated.

Alchemy III, a molecular modeling program marketed by Tripos Associates, was used to calculate the molecular dimensions of the phthalocyanine molecules.

Results and Discussion

Table I summarizes physical data on all samples, including information from X-ray powder diffraction, microanalysis, and surface area measurements.

Cationic Clays. Intercalation compounds of hectorite clays and cationic phthalocyanines were prepared by hydrothermal treatment of silica sol, magnesium hydroxide, lithium fluoride, and the Pc. Figure 2 shows typical X-ray diffraction patterns for both an oriented thin film of synthetic alcian blue, pyridine variant-hectorite, and a powdered sample of synthetic 15-crown-5 phthalocyanine-hectorite. The height of the gallery region is given by the d(001) spacing which is the peak corresponding to the lowest 2θ value. Thin film samples represent preferred

orientations such that (00*l*) reflections are enhanced. Although oriented films of synthetic clays display intense (001) peaks, other (00*l*) reflections are generally not observed, indicating a low degree of long-range ordering. The powder patterns are generally much weaker than the oriented films, but they display the indicative clay reflections at 19.6° 2θ (4.52 Å) and 35.1° 2θ (2.56 Å) corresponding to the (110,020) and (130) reflections, respectively. These (*hk*) reflections in synthetic products display typical Warren line shapes[14] in that they are weak and asymmetric, tailing off to higher 2θ values. According to the mathematical treatment by Warren,[14] the breadth of the peak is inversely porportional to the particle size. In other words, the broader the peak, the smaller the particle size, and therefore a higher surface area is expected. The broad peak near 12° 2θ is either much weaker or not observed at all in the other synthetic products, and it remains unassigned at this time. Note that there is no indication of unreacted Mg(OH)$_2$. If the reaction were not complete, very intense and narrow peaks would occur at 18.6° 2θ and 38.0° 2θ for the (001) and (101) reflections, respectively, of the magnesium hydroxide mineral brucite. It is also absent from thin-film patterns of unwashed products.

Hydrothermal crystallization of hectorites in the presence of water-soluble porphyrins and metalloporphyrins has been demonstrated recently,[2] and the layering process was followed by small-angle neutron-scattering (SANS) techniques. The generally accepted mechanism of formation of hectorite, which was supported by the SANS study, proposes the condensation of tetrahedral silicate layers on pre-existing brucitic sheets. Since porphyrins with peripheral cationic charges were used, similar to the phthalocyanines of the current study, they are incorporated in the clay structure as the gallery exchangeable cations. Although 15C5Pc is not cationic, protonation of the inner, non-metallated macrocycle may occur upon incorporation. In support of this, protonation of porphyrins on clay surfaces has been observed and studied extensively.[15]

Microanalysis data collected in Table I demonstrate that a substantial amount of phthalocyanine is incorporated into both synthetic and ion-exchanged clays. All materials are highly colored. Comparison of theoretical to experimental C/N ratios reveals that the phthalocyanine macrocycles have been incorporated intact. By comparing the size of the gallery spacing with the dimensions of the gallery cation, one can determine the orientation of the guest species within the gallery. The size of an underivatized phthalocyanine (or copper Pc) molecule has been reported[16] to be 12.5 × 9.9 × 4.7 Å^3. Addition of isothiuronium groups to CuPc forms the dye alcian blue (AB), and addition of pyridyl groups makes the AB pyridine variant. Such additions increase the size of the molecules to approximately 21.6 × 19.0 × 9 Å^3 and 20.6 × 18.0 × 10 Å^3 for AB and AB,pyridine, respectively.[17] The large "thickness" is a result of the orientation of the side groups above and below the plane of the Pc ring in

a "free" molecule with unrestricted motion. The confining interlayer region of a clay is expected to force these units into a more planar arrangement, as is observed for porphyrin molecules.[2,18] The *d* spacing must therefore correspond to the plane of the phthalocyanine molecule lying parallel to the silicate layers within the gallery region since the gallery height ranges from only 4.4 to 6.1 Å.

Synthetic hectorites and corresponding ion-exchanged natural hectorites at dilute dye concentrations share similar physical properties in most cases. Their surface areas are high: 167–213 and 64–65 m^2/g, respectively; values are especially high for the synthetic samples due to their small particle size (as discussed earlier). In addition, the samples share similar levels of organic uptake as seen by their organic ion exchange capacities (23–36 mequiv/100 g). The hectorites exchanged at a high dye concentration display extremely low surface areas (<5 m^2/ g). Corresponding microanalysis data yield organic ion exchange capacities of 90–110 mequiv/100 g, which are in excess of the reported[19] cation exchange capacity of natural hectorite (80 mequiv/100 g). It is therefore likely that the clay layers, now packed with dye molecules, are dense to nitrogen adsorption. In addition, a suggestion[20] that clay aggregates coated with dye molecules exist at high dye concentrations may also apply. UV–visible absorption behavior of the synthetic dye–clay complexes will be performed in future experiments in order to probe whether this aggregation occurs.

Hectorite samples of 15-crown-5 tetrasubstituted phthalocyanine (15C5Pc) display some variation in terms of *d*(001) spacings. The value of 18.6 Å for the concentrated 15C5Pc–SHCa is significantly higher than those for the samples with a lower loading of Pc (16.0–16.6 Å). Gallery heights therefore range from 6.4 to 9.0 Å. Molecular modeling predicts the size of 15C5Pc to be 19.7 × 17.1 × 10 Å^3. The large vertical dimension of 15C5Pc is a result of the puckered conformation of the crown ether macrocycles above and below the plane of the Pc ring in a "free" molecule of unrestricted geometry. From these values 15C5Pc, like the Pc-hectorites previously discussed, must also be oriented parallel to the silicate clay layers. Again, interlayer confinement probably causes the 15-crown-5 substituents to lie in a more planar arrangement. The higher *d*-spacing of the concentrated sample 15C5Pc-SHCa at 18.6 Å may suggest that a slight degree of tilting occurs in order to accommodate the greater number of molecules present. The directly crystallized synthetic sample has a high surface area at 213 m^2/g, while the ion-exchanged samples are both extremely low (<5 m^2/g). Such behavior can be correlated to the degree of Pc incorporation, as reflected by the microanalysis data. The former sample has just 5.3 wt % C, while the others have from three to five times as much (13.7–26.2 wt % C). Like the AB-SHCa samples with a concentrated extent of dye, the clay samples with so much 15C5Pc also have layers that are densely packed with phthalocyanine molecules.

Further speculation about the nature of this intercalation is difficult because questions remain about the ionic character of 15C5Pc upon interaction with a clay, whether by direct crystallization or ion-exchange. The possible

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modes are (a) the inner macrocycle protonates to the mono- or dication, (b) the crown ether units complex a charge-balancing cation, or (c) a combination of the two factors. Some information about this mechanism will be probed by UV-visible absorption spectroscopy in future experiments. This technique has been used, for example, to monitor the effects of alkali metal cations complexed in the crown groups of 15C5Pc.[12] Previous workers[8-10] have concluded that crown ethers and cryptands complex interlayer cations upon incorporation in smectite clays. However, these studies were carried out in methanol rather than water because of the much stronger cation solvation by water, compared to methanol, with which the polyether has to compete.[21] Sodium ions are present in the natural hectorite SHCa, and Li^{+} ions are present in the galleries of the synthetic clay (in addition to any organic template). Lithium(I) ions have such a strong polarizing effect that a substitution of their hydration shell by a crown ether is almost never observed.[21] There remains the possibility of some limited complexation of Na^{+} by the 15C5 units in the natural hectorite ion-exchanged materials.

Anionic Clays. Complexes of a layered double hydroxide and an anionic phthalocyanine were formed both by ion exchange and directly by hydrolysis of mixed solutions of aluminum nitrate, magnesium nitrate, and copper(II) phthalocyaninetetrasulfonate (CuPcTs) with a solution of sodium hydroxide. Figure 3 shows X-ray diffraction patterns of a Mg-Al-NO$_3$ LDH film, a film of ion-exchanged CuPcTs-LDH, and a powder pattern of synthetic CuPcTs-LDH. Because of the rhombohedral packing of the LDH unit cell,[22] ABCABC-type stacking causes (hkl) reflections along the c axis to occur in increments of (003). The (00l) peaks are shifted to lower 2θ values upon incorporation of the large CuPcTs anion, compared to the pattern of LDH with the small interlayer NO$_3^-$ anion. For the synthetic CuPcTs-LDH, the most acceptable assignment for all the observed XRD peaks is to index using cell dimensions[23] of $a_0 = 3.05$ Å and $c_0 = 69$ Å. The peak at lowest observed 2θ is then assigned as (003) and the rest as its higher harmonics (except for the (102) reflection), and an average of 23 Å for the basal spacing is obtained. Any other attempt does not incorporate all of the peaks: neither assigning the 11.3- or 7.6-Å peaks as the (003), nor describing the powder pattern as a mixture of nitrate-, carbonate-, and CuPcTs-containing LDHs is completely satisfactory. The powder pattern of ion-exchanged CuPcTs-LDH is similar to that of the synthetic sample, although there are small differences that can be seen from Table II; the most intense peak is now the (009) reflection as opposed to the (006), and the (00 12) is not observed.

Molecular modeling was exploited to ascertain how the gallery spacing is consistent with various orientations of the phthalocyanine molecule. The dimensions of CuPcTs are calculated[17] to be 19.9 × 17.3 × 5.5 Å[3]. A gallery height of 18.2 Å is determined for CuPcTs-LDH by subtracting the LDH brucite layer itself (4.8 Å) from the basal spacing of 23 Å. This spacing allows CuPcTs to have its long axis oriented perpendicular to the clay layers. This arrangement is also consistent with the amount of uptake of the macrocycle in LDH as reflected in the microanalysis results. The exchange capacities of LDHs are generally
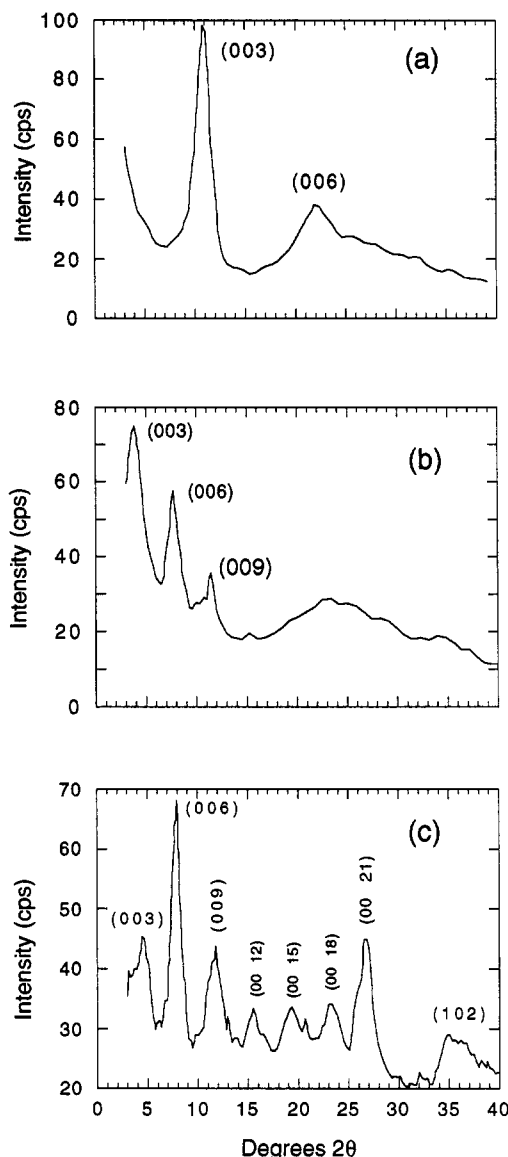
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(22) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369.
(23) Miyata, S.; Okada, A. *Clays Clay Miner.* **1977**, *25*, 14.

Figure 3. X-ray powder patterns of (a) a thin film of Mg-Al-NO$_3$ LDH, (b) a thin film of ion-exchanged CuPcTs-LDH, and (c) a powder pattern of synthetic CuPcTs-LDH; (hkl) reflections are assigned as indicated.

quite high because of their high layer charge densities. For instance, Mg-Al-NO$_3$ LDH has a reported layer charge density[24] of 32.4 Å^2/charge. This type of density is possible for cationic clays only in the case of micas (32-34 Å^2/charge). The calculated anion exchange capacity (aec) of the Mg$_{0.75}$Al$_{0.25}$(OH)$_2$(NO$_3^-$)$_{0.25}$ LDH prepared in this study is 218 mequiv/100 g of clay, which compares with ca. 80 mequiv/100 g for a hectorite-type cationic clay. From the 20.5 wt % carbon in syn-CuPcTs-LDH determined by microanalysis, the calculated uptake of CuPcTs is 214 mequiv/100 g of LDH, or 98% of theoretical. The aec is less for the ion-exchanged sample at 179 mequiv/100 g, or 82% of theoretical, with the remaining sites probably taken up by nitrate or carbonate anions. High degrees of organic anion exchange, on the order of 80-100%, are very common[24] for LDHs. The only way to pack so many large phthalocyanine molecules on the available area of exchange sites in LDH is for them to be oriented in a tilted arrangement with respect to the hydroxide layers. If the

(24) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201.

Table II. Indexing of X-ray Diffraction Patterns for Various Layered Double Hydroxides in Powdered Form (d Spacings in Å)[a]
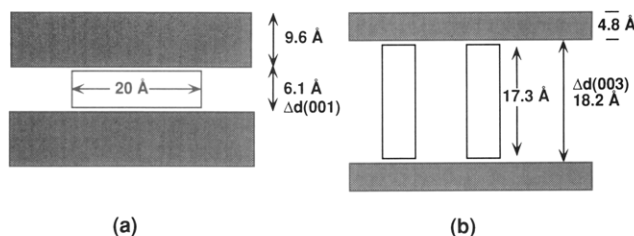
sample	d_{obs}	I/I_0	d_{calc}	(hkl)
Mg–Al–NO$_3$	8.17	100	8.17	003
	4.04	38	4.08	006
	2.61	38	2.59	102
	2.35	24	2.32	105
ion exchanged	23.0	84	23.0	003
CuPcTs–LDH	11.4	81	11.5	006
	7.77	100	7.67	009
	4.52	47	4.60	00 15
	3.88	48	3.83	00 18
	3.42	48	3.28	00 21
	2.60	48	2.59	102
synthetic	22.5	70	23.0	003
CuPcTs–LDH	11.5	100	11.5	006
	7.65	65	7.67	009
	5.73	45	5.75	00 12
	4.62	45	4.60	00 15
	3.87	45	3.83	00 18
	3.33	65	3.29	00 21
	2.57	35	2.59	102

[a] d_{obs} = observed reflections; I/I_0 = relative intensities; d_{calc} = calculated spacings; (hkl) = indices for reflections (a_0 = 3.05 Å); LDH = Mg–Al–NO$_3$ layered double hydroxide; CuPcTs = Cu(II) phthalocyaninetetrasulfonate.

molecules were lying flat, an area of 86 Å^2 would be required per unit charge (19.9 Å × 17.3 Å/4 charges). However, if a perpendicular orientation with the long axis is assumed, then the calculated layer charge density of 25 Å^2/charge (18.2 Å × 5.5 Å/4 charges)[25] more closely matches the reported value of 32 Å^2/charge.

The incorporation of phthalocyanines into layered double hydroxides has in the past proven quite difficult. This paper represents the first results of a directly crystallized Pc–LDH compound; in this case, the Pc is incorporated directly in the gel as the layers crystallize. In terms of ion exchange, until recently the only previously reported material was NiPcTs in a Li–Al LDH. This material was reported to have a gallery height[26] of just 5.8 Å which indicates a parallel orientation, a surprising result considering that the layer charge density of Li–Al LDH is nearly identical (33 Å^2/charge) to that of Mg–Al LDH. More recently, another synthetic approach for preparing CoPcTs-exchanged LDH materials has been reported.[27] In this route, a Mg–Al–CO$_3$ LDH is converted to a metal oxide solid solution at 500 °C and is then exposed to excess aqueous Pc salt at 60 °C. The method reported here for preparing ion-exchanged Pc–LDH compounds does not need to exploit the first heating step. In this method a freshly prepared layered double hydroxide is never allowed to dry out, which allows for maximum interlayer separation in order to accommodate the large Pc molecules. A similar approach was very recently demonstrated for pillaring LDH with polyoxometalates.[28] XRD results indicate that this "wet" method for preparing ion-exchanged Pc–LDH provides samples superior in crystallinity to even the directly crystallized so-called "synthetic" sample.

On the basis of basal spacings, ionic size, layer charge density, and anionic exchange capacity, it is evident that

(25) The gallery height of 18.2 Å is used for this calculation because it appears to reflect an average in the length and width of the Pc molecule (actual average: 19.9 × 17.3/2 = 18.6 Å).

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(28) (a) Wang, J.; Tian, Y.; Wang, R.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 1276. (b) Wang, J.; Tian, Y.; Wang, R.; Colon, J. L.; Clearfield, A. *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 63.

Figure 4. Schematic representation of the arrangement of phthalocyanine molecules (a) alcian blue, pyridine variant in hectorite cationic clay and (b) copper(II) phthalocyaninetetrasulfonate in Mg–Al layered double hydroxide anionic clay.

the CuPcTs anions are arranged with their molecular axes perpendicular to the brucitic hydroxide layers of Mg–Al LDH. There are several precedents for intercalants arranged in the gallery region with their axes perpendicular, or nearly so, to the hydroxide layers of LDHs. These include fatty acid anions, dicarboxylates, and alkyl sulfates,[24,29] in addition to the organic dyes indigo carmine and new coccine,[6] and tetrakis(4-sulfonatophenyl)porphyrin.[3] The overall size and charge of the latter porphyrin molecule compares well to the CuPcTs of this study, and it was also intercalated into a Mg–Al-type layered double hydroxide (anions = Cl$^-$).

The observed surface area of Mg–Al–NO$_3$ LDH is unexpectedly low at only about 2.5 m^2/g. Miyata[22] reported a value of approximately 10 m^2/g for this sample, but literature values tend to vary widely for Mg–Al LDHs dependent upon not only the anion but on the crystallization conditions. For example, Miyata has observed a range in surface area from 5–110 m^2/g (anion = SO$_4^{2-}$ and ClO$_4^-$, respectively,[23,22] with the majority falling in the range 5–25 m^2/g (anion = CO$_3^{2-}$, CrO$_4^{2-}$, Cl$^-$).[5,22,23] Drezdzon has calculated an expected surface area of 20–40 m^2/g (assuming 125 °C outgassing) and observed values in this region.[3] Reichle[31] discovered that smaller, thin crystals displayed a very high surface area of 120 m^2/g as compared to only 14 m^2/g for large hexagonal crystals; the former crystals formed at 65 °C while the latter formed at 200 °C under pressure. Outgassing conditions for N$_2$ BET surface area measurements are also similar. The crystallization conditions reported here are comparable to previous studies in terms of concentrations, temperature, and time. Nonetheless, it is evident that a larger crystal size occurs under these synthetic conditions. Surface areas did not become appreciable for Mg–Al–NO$_3$ LDH until outgassing was performed at 500 °C for 24 h when a value of 140 m^2/g was obtained. It is well-known[22] that a high surface area MgO phase forms from 400–600 °C in these materials due to dehydration and loss of CO$_2$.

Conclusions

Phthalocyanines can be directly incorporated into the gallery regions of both cationic and anionic clays as the layers crystallize from solution under hydrothermal conditions. The Pc contents correspond well to the expected exchange capacities of both the synthetic clays and their analogous ion-exchanged counterparts. The orientation arrangement of the large, flat Pc macrocycles differs for cationic and anionic clay systems. For the cationic clays

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examined in this study, whether copper(II) phthalocya-
nines are incorporated directly during hydrothermal
crystallization or via ion exchange, they are aligned parallel
to the clay layers. On the other hand, Cu(II)–Pc's appear
to be tilted perpendicular to the brucite layers of layered
double hydroxides whether they are incorporated directly
or via ion exchange. These arrangements are displayed
schematically in Figure 4. There is considerable interest
in stacked metal-over-metal structures of phthalocyanines
as novel conducting materials,[32] and the gallery regions of
clays provide opportunities for such stacking arrange-

ments. This postulate warrants further study into the
possibility of metal-metal interactions between adjacent
molecules.

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B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1985,** *107,* 6915.