Anion Intercalation and Exchange in Al(OH)₃-Derived Compounds

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Precipitation of Al^{3+} at pH = 10 in excess Li_2CO_3 leads to an anion exchanging compound, $[Al_2Li(OH)_6]_2^+CO_3^{2-}$. This compound exhibits, compared to $[Mg_3Al(OH)_8]_2^+CO_3^{2-}$, a higher degree of size selectivity in anion exchange. The structure of the $[Al_2Li(OH)_6]^+$ layers is gibbsite-like, with a (110) diffraction feature at $d = 4.35$ Å indicating a pronounced Al^{3+} ordering. As claimed originally by Serna et al., the structure is $[Al_2Li(OH)_6]^+A_{1/z}^{z-}$ rather than $[Al_2(OH)_6]Li^+A_{1/z}^{z-}$, with the Li^+ coordinated in the octahedral positions left vacant by Al^{3+}. This emerges from the details of a lithium-leaching process, which proposedly leads to a novel compound, $[Al_2H(OH)_6]^+A_{1/z}^{z-}$. © 1985 Academic Press, Inc.

Introduction

In a recent publication, Serna et al. (1) report on the synthesis of $[Al_2Li(OH)_6]_2$ CO_3, and they assess that this compound exhibits hydrotalcite-like properties. Hydrotalcites consist of positively charged brucite-type layers, $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$, which intercalate and exchange anions. The synthetic work of Feitknecht (2), the XRD studies of Allmann (3) and Taylor (4), the physicochemical studies of Miyata (5), and the catalytic work of Reichle et al. (6) almost exhaustively summarize our knowledge regarding these rather interesting compounds. They form, in terms of charges, the mirror image of clays and exhibit, for inorganic compounds, the unique property of anion exchange. The aforementioned claim of Serna et al. (1) when substantiated would actually extend the class of inorganic anion exchangers from $M^{II}M^{III}$ compounds to $M^{III}M^I$ compounds.

The present study seeks to verify two key aspects of the claim of Serna et al. (1): (i) the structure of the compounds, specifically coordination of Li^+ in the octahedral positions within the Al(OH)₃ layer (leading to $[Al_2Li(OH)_6]^+A_{1/z}^{z-}$) rather than between adjacent Al(OH)₃ sheets (leading to $[Al_2(OH)_6]Li^+A_{1/z}^{z-}$) and, (ii) the anion-exchanging property of the compounds.

This work is part of a broader program, which only recently has been initiated. One of its objectives is to learn more about the role of solvation in intercalation and swelling of layered compounds through a side-by-side comparison of cation exchange and anion exchange. The other objective is to explore the technological potential of layered inorganic anion exchangers in fields such as selective sorption of weak acids (e.g., CO_2, H_2S etc.), selective anion exchange (e.g., CN^-, PO_4^{3-}), anion conduc-
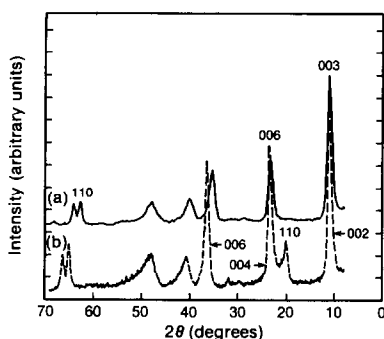
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FIG. 1. The main difference between the XRD patterns of $[Mg_3Al(OH)_8]_2CO_3$ (a) and $[Al_2Li(OH)_6]_2CO_3$ (b) is a feature around 20.30 degrees in (b).

tance, gelation, and intracrystalline base catalysis.

Experimental

Materials. Analytical reagent grade compounds were used for all preparations described in this work. Water used for synthesis was distilled and then passed through a demineralizer.

Synthesis. The preparation of $[Al_2Li(OH)_6]^+ A^{z-}_{1/z}$ (A^{z-} = CO_3^{2-}, SO_4^{2-} and $Fe(CN)_6^{4-}$) followed closely Serna *et al.* (*1*), which uses a variation on the method described originally by Feitknecht (*2*). A total amount of 250 ml of a 0.4 M $AlCl_3 \cdot 6H_2O$ solution was added dropwise to 600 ml of a mixture of 1.5 M LiOH $\cdot$ H_2O and (0.16/z) M Na_zA. The pH varied during addition from ~13 (initially) to 10.2 (finally). Vigorous stirring was maintained throughout the approximately 45-min addition period. The gel-type precipitate, which formed instantaneously, was left overnight for further ripening under gentle stirring, and then separated from the supernatant solution by either filtration or centrifugation. Occasionally, we performed a hydrothermal treatment (59 hr at 160°C) in the supernatant solution before separation. Prior to XRD or other measurements, the products were washed with an excess of hot deionized water, and dried at 70°C for about 15 hr. For

$A^{z-} \neq CO_3^{2-}$ care had to be taken to exclude CO_2/CO_3^{2-} from the source chemicals and from the ambient during precipitation/drying. Yields generally were within 80–95% of the stoichiometrically expected ones.

Instrumentation. The XRD patterns were recorded on a powder diffractometer (General Electric). Cu$K\alpha$ radiation was obtained from a copper-target tube operated at 40 kV, 20 mA, utilizing an additional graphite diffracted-beam monochromator.

IR spectra were recorded from KBr (4000–400 cm^{-1}) and CsI (400–200 cm^{-1}) pellets, employing a concentration of 2 mg sample per 200 mg salt, and utilizing a wavelength-dispersive spectrometer (Perkin–Elmer Model 683).

Cation (Li$^+$, Na$^+$, and K$^+$) analyses were performed via atomic absorption. The samples were digested at pH = 3.2 in a solution of 10% HCl. For atomic absorption (AA) measurements we used a Perkin–Elmer Model 380 atomic absorption spectrophotometer.

Results and Discussion

Structure. The XRD pattern of $[Al_2Li(OH)_6]_2CO_3$ is very similar to that of $[Mg_3Al(OH)_8]_2CO_3$, synthetic hydrotalcite (Fig. 1).
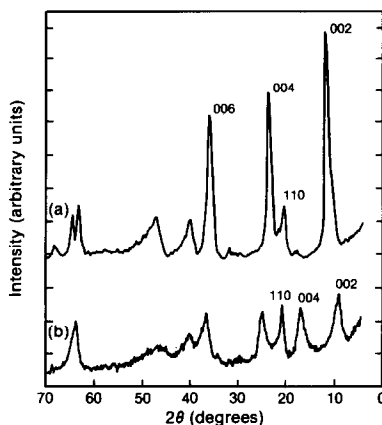
FIG. 2. XRD Patterns of $[Al_2Li(OH)_6]_2CO_3$ (a) and $[Al_2Li(OH)_6]_4Fe(CN)_6$ (b). The 20.30-degree feature shows up in both patterns.

TABLE I

INDEXING^a OF THE XRD PATTERNS (8) OF [Al$_2$Li(OH)$_6$]A^{z-} (A^{z-} = CO$_3^{2-}$, SO$_4^{2-}$, Fe(CN)$_6^{4-}$)

CO$_3^{2-}$			SO$_4^{2-}$			Fe(CN)$_6^{4-}$		
d-spacing (Å)		hkl	d-spacing (Å)		hkl	d-spacing (Å)		hkl
Obs.	Calc.^{b}		Obs.	Calc.^{b}		Obs.	Calc.^{b}	
7.56	7.55	002	8.19	8.19	002	10.04	10.04	002
4.35	4.38	110	4.87	4.84	011	5.25	5.02	004
3.77	3.78	004	4.42	4.38	110	4.31	4.38	110
2.51	2.52	006	4.40	4.10	004	2.46	2.46	022
2.25	2.25	016	2.52	2.51	021	2.22	2.22	314
1.98	1.99	017	2.26	2.26	206	2.01	2.02	026
1.47	1.46	330	1.47	1.48	228	1.46	1.46	330
1.44	1.44	600	1.45	1.46	330	—	—	—

^{a} Utilizing a monoclinic unit cell with a = 8.68 Å, b = 5.07 Å, and c = 15.12, 16.40, and 20.10 Å for CO$_3^{2-}$, SO$_4^{2-}$, Fe(CN)$_6^{4-}$, respectively.

^{b} The values of β used in these calculations were 92° 56′, 92° 42′, and 92° 12′ for CO$_3^{2-}$, SO$_4^{2-}$, and Fe(CN)$_6^{4-}$, respectively. These were estimated from geometrical considerations assuming a constant horizontal displacement of adjacent hydroxyl layers as in gibbsite whose β is 94° 34′.

The main difference is a diffraction feature around 2θ = 20.30° in [Al$_2$Li(OH)$_6$]$_2$CO$_3$. This diffraction feature has also been observed by Serna et al., and tentatively indexed as (101) in a (pseudo) hexagonal unit cell (1). Figure 2 compares the XRD patterns of [Al$_2$Li(OH)$_6$]$_2$CO$_3$ and [Al$_2$Li(OH)$_6$]$_4$Fe(CN)$_6$. It emerges that [Al$_2$Li(OH)$_6$]$^+A^{z-}_{1/z}$ has a layered structure (pronounced basal reflections), with the layer distance following closely the size of the intercalated anion. Furthermore, the compounds do not exhibit a pronounced tendency to swell in moist atmosphere, whereas the smectites do (7). We infer that this difference with the smectites derives from the low energy of solvation of anions compared to cations. Therefore, it is not surprising that with respect to interplanar spacing versus anion size, the structural properties of the Al- and Li-based compounds closely mimic those of the synthetic hydrotalcites (see, however, "Anion Exchange," below).

The feature around 2θ = 20.3° turns out to be highly independent of the spacing between the basal planes. Accordingly we have indexed it as (110). Actually, gibbsite, Al(OH)$_3$, itself has a pronounced d = 4.85 Å feature, due to the strict ordering of the Al^{3+} cations. Accordingly, Table I indexes the diffraction features of [Al$_2$Li(OH)$_6$]$^+A^{z-}_{1/z}$ (A^{z-} = CO$_3^{2-}$, SO$_4^{2-}$, and Fe(CN)$_6^{4-}$) in the monoclinic unit cell appropriate for gibbsite rather than the hexagonal unit cell relevant for hydrotalcites.

The shape of the diffraction features around 20, 40, and 50° (Fig. 1), with their relatively sharp onset at low 2θ and tail towards higher 2θ, is characteristic of turbostratic disorder (9). This disorder takes away significance from indexing the Al and Li compounds in a gibbsite-like two layer structure (Table I, corresponding to a hydroxyl stacking AB–BA/AB–BA/etc.), and it introduces significant uncertainty into the value quoted for the angle β.

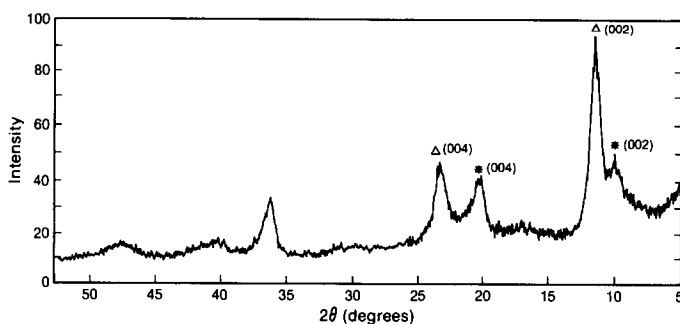In summary, the main features emerging

FIG. 3. Partial exchange results in different distances for SO_4^{2-} intercalation (*) and CO_3^{2-} intercalation ($\triangle$).

from the XRD patterns are: $[Al_2Li(OH)_6]^+$ $A_{1/z}^{z-}$ has a layered structure exhibiting turbostratic disorder with a structure of the individual layers closely similar to gibbsite, i.e., with ordering of the Al^{3+} cations. The distance between the layers, as in synthetic hydrotalcite, closely follows the size of the unsolvated intercalated anions.

Anion Exchange. Room-temperature exposure of $[Al_2Li(OH)_6]_2CO_3$ to an excess of a pH = 3.2 solution of Na_2SO_4 gives rise to anion exchange. The XRD pattern of a partially exchanged sample is shown in Fig. 3, and the exchange isotherm based on XRD data in Fig. 4.

Both the XRD pattern and the shape of the exchange isotherm are indicative of the fact that CO_3^{2-} and SO_4^{2-}, anions with approximate 1-Å difference in size, do not coexist within the same interlayer. This is what is to be expected on the basis of exchange of cations of different sizes in, for example, layered phosphates (*10, 11*). We would like to point out that, although the exchange isotherm is being based on XRD data, we actually are dealing with two independent indications for a lack of coexistence of CO_3^{2-} and SO_4^{2-}, i.e.:

(a) the *position* of the XRD lines (split basal reflections, Fig. 3);

(b) the variation in *relative intensity* of the XRD lines, as summarized in Fig. 4.

Surprisingly, Miyata (*5*) reports for exchange of anions of approximately 1-Å size

difference in hydrotalcites shapes of exchange isotherms which are close to Langmuirian. This is indicative of the coexistence of anions with different radii in the same interlayer. Compared to the (Mg,Al)-based hydrotalcites the (Al,Li)-based compounds apparently have a higher selectivity in discriminating between anions of slightly different size. We propose that this difference originates in the higher density of the layer charge of the (Al,Li) compounds when compared to (Mg,Al) compounds (c.f. $[Mg_3Al(OH)_8]^+$ with $[Al_2Li(OH)_6]^+$). A higher charge density is expected to lead to a sharper dependence of intercalation energy on intercalate size.

Lithium "Siting." As an alternative to a structure with positively charged layers, $[Al_2Li(OH)_6]^+A_{1/z}^{z-}$, one might consider the intercalation of the neutral salt Li_zA be-
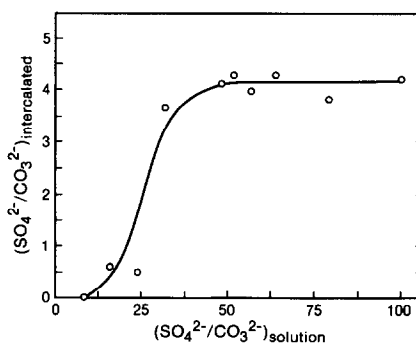

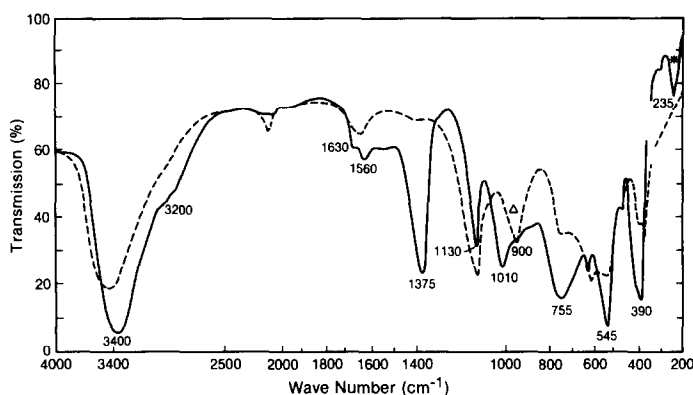FIG. 4. Anion exchange isotherm, i.e., intercalated versus solution (SO_4^{2-}/CO_3^{2-}).

FIG. 5. IR spectra of [Al₂Li(OH)₆]₂SO₄ (—) prior and (---) after Li leaching. The band marked (*) is being assigned to a Li–O-derived vibration (1, 13) and the band marked (△) to a $O^{\delta-}$--H^+--$O^{\delta-}$ derived vibration (14–17).

tween neutral Al(OH)₃ layers, [Al₂(OH)₆]Li$_z$A (12). Seemingly in agreement with "intersalation" of a neutral salt is our observation that prolonged hydrothermal treatment of [Al₂Li(OH)₆]₂SO₄/Na₂SO₄ and [Al₂Li(OH)₆]₄Fe(CN)₆/K₄Fe(CN)₆ leads to a loss of 80% of all Li$^+$ cations. Further to the location of the Li$^+$ cations, the following observations are considered to be relevant:

(1) Lithium-leaching up to 80% does not lead to significant change in the XRD patterns;

(2) AA convincingly shows that the loss of Li$^+$ is not being compensated by a gain of Na$^+$ (or K$^+$);

(3) A synthesis procedure in which precipitation of Al^{3+} with LiOH/Li₂CO₃ was replaced by precipitation with NaOH/Na₂CO₃ did not lead to [Al₂Na(OH)₆]₂CO₃ or [Al₂(OH)₆]Na₂CO₃, but rather to poorly crystalline gibbsite, Al(OH)₃;

(4) Concurrent with the leaching-away of Li$^+$ the 235-cm^{-1} IR band goes down in intensity, whereas a new band around 920 cm^{-1} comes up (Fig. 5).

From Observation 1 we conclude that Li$^+$ removal is not merely the removal of intercalated salt:

$$[Al_2(OH)_6]Li_zA \rightarrow [Al_2(OH)_6] + Li_zA$$
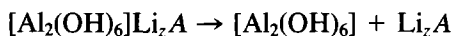
Observation 2 demonstrates that Li$^+$ removal cannot be ascribed to cation exchange of an intercalated salt:

$$[Al_2(OH)_6]Li_zA + (Na^+)_{soln} \rightleftharpoons$$

$$[Al_2(OH)_6]Na_zA + (Li^+)_{soln}$$
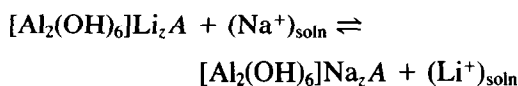
Actually, the Li$^+$ removal without an accompanying structural change has, for reasons of charge balance, to be compensated by the introduction of another cation. On the strength of our AA analysis (Observation 2) we have to conclude that the replacement of Li$^+$ is one by H$^+$. This inference is being supported by the IR Observation 4. A frequency close to 900 cm^{-1} is what previously has been reported for similar $O^{\delta-}$ . . . H$^+$ . . . $O^{\delta-}$ derived vibrations (Table II).

We conclude that, upon Li$^+$ leaching, other alkali metal ions are being selectively rejected in favor of H$^+$. We interpret this as a cation-size effect, due to the location of the Li$^+$ cation (e.g., the cation vacancy left behind) in the octahedral cation positions within the Al₂(OH)₆ layer. Treating the structure of the individual Al₂(OH)₆ layers as close packed "spheres" with $r_{OH^-} \approx 1.45$ Å, the $r+/r- \leq \sqrt{3} - 1$ radius-ratio guideline for octahedral cation coordination (18) indicates the Na$^+$ cation to be too large to

TABLE II

COMPARISON OF νOHO IN SOME PROTON BONDED IONIC SPECIES

Ion	νOHO (cm^{-1})	Reference
$[Al_2H(OH)_6]_2^+ SO_4^{2-}$	900	This work
$[Al_2H(OH)_6]_4^+ Fe(CN)_6^{4-}$	940	This work
$(H_2O\,H\,OH_2)^+$	980	(14)
$CH_3(NH_2)COHOC(NH_2)CH_3^+$	800	(15)
$(O_2NOHONO_2)^-$	800	(16)
$(RCO_2HO_2CR)^-$	800	(17)

enter. This is supported by Observation 3, i.e., a lack of coprecipitation of Na$^+$.

In summary, Observations 1–4 are consistent with the location of Li$^+$ in the octahedral positions left vacant by Al^{3+} (c.f. the mineral hectorite (19), in which Mg^{2+} is being partly replaced by Li$^+$), they confirm the earlier claim of Serna et al. (1), and they indicate the production of a novel compound, $[Al_2H(OH)_6]^+ A_{1/z}^{z-}$, upon Li$^+$ leaching:
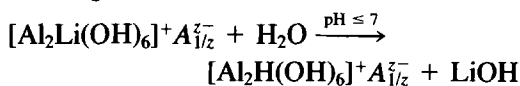
$$[Al_2Li(OH)_6]^+ A_{1/z}^{z-} + H_2O \xrightarrow{\text{pH} \leq 7}$$
$$[Al_2H(OH)_6]^+ A_{1/z}^{z-} + LiOH$$

Acknowledgments

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