

## CRYSTAL-CHEMICAL STUDY OF LAYERED $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^- \cdot n\text{H}_2\text{O}$

CARLOS J. SERNA, JOSE L. RENDON,<sup>1</sup> AND JUAN E. IGLESIAS

Grupo de Fisico-Química Mineral, C.S.I.C., Serrano, 115-dpdo. Madrid-6, Spain

**Abstract**—A layered double hydroxide with a chemical composition  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^- \cdot n\text{H}_2\text{O}$ , where  $\text{X}^-$  is an interlayer anion, has been synthesized hydrothermally at 130°C from aluminum-tri-(sec-butoxide) and lithium carbonate. Electron micrographs showed the product to have a platy morphology with distinct hexagonal symmetry, which has been corroborated by selected area electron diffraction patterns corresponding to a projection of the structure on its (001) plane. Evidence for a superlattice with  $a = 5.32 \text{ \AA}$  was obtained, indicating cation ordering among octahedral sites. X-ray powder diffraction data also can be interpreted by reference to a hexagonal supercell with dimensions  $a = 5.32 \text{ \AA}$  and  $c = 15.24 \text{ \AA}$ . The arrangement of the octahedral sites appears to be that of gibbsite, but with the vacancies filled with lithium cations. Anions must be present between the sheets to balance the charge. A complete assignment of the observed infrared lattice vibrations can be made for the anion  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$  with the ideal  $D_{3h}$  symmetry for motions within one octahedral sheet. The results show that  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^- \cdot n\text{H}_2\text{O}$  is a hydrotalcite-like compound with the octahedral cations largely ordered. The general formula for hydrotalcite-like compounds,  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^+\text{X}^{m-}_{x/m} \cdot n\text{H}_2\text{O}$ , should be extended to include the monovalent lithium cation.

**Key Words**—Double hydroxide, Electron diffraction, Hydrotalcite, Infrared spectroscopy, Lithium.

### INTRODUCTION

A considerable literature has appeared on layered double-hydroxides formed by coprecipitation of di- and trivalent cation salt solutions (e.g., Miyata, 1975; Brindley and Kikkawa, 1979; Taylor, 1969). The structure of these materials consists of positively charged brucite-like layers with interlayer anions and water molecules. Their chemical compositions have been represented by the formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^+\text{X}^{m-}_{x/m} \cdot n\text{H}_2\text{O}$ , where  $\text{M}^{2+} = \text{Mg}, \text{Fe}, \text{Ni} \dots$ ;  $\text{M}^{3+} = \text{Al}, \text{Fe} \dots$ ;  $\text{X}^{m-} = \text{OH}^-, \text{Cl}^-, \text{ClO}_4^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{CrO}_4^{2-} \dots$ , and  $x$  is 0.20–0.33. However, for natural minerals  $x$  seems almost to be restricted to 0.25 (Taylor, 1973). Recently, Bish (1977, 1978a, 1980) showed that anion-exchange reactions are possible for these compounds.

In a study of the hydrolysis of  $\text{Al}^{3+}$  in the presence of carbonate salt solutions with monovalent cations, a compound with the structure described above was obtained for the lithium cation (Serna *et al.*, 1977) with a composition  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ . This result suggests that the general formula for layered double hydroxides should be extended to include this compound. In the present paper, attention is paid to the crystallochemical properties of this compound, particularly the nature of its octahedral sheet. The effect of molecular vibrations of different anions in the interlamellar space on the lattice dynamics will be reported elsewhere.

### EXPERIMENTAL

A benzene solution of aluminum-tri-(sec-butoxide) (ASB), 15% W/V, was added dropwise to a lithium car-

bonate aqueous solution with an Al/Li ratio  $< 2$ . An excess of lithium carbonate was necessary to avoid aluminum hydroxides in the precipitate. Hydrolysis of the ASB was continued for periods of 4 to 20 hr (Serna *et al.*, 1977). The same Al-Li double-hydroxy carbonate was obtained by slow addition of an aluminum carbonate solution (0.5 M) to a saturated LiOH solution down to pH 10. In both experiments the gels were treated hydrothermally for several days at about 130°C to improve particle size. The products were later washed to eliminate excess  $\text{Li}_2\text{CO}_3$  or LiOH.

The same procedures were used to synthesize  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$  compounds with different anions. Furthermore, homoanionic samples were also obtained by anion-exchange reactions. However, because the greatest crystallinity was observed for the carbonate anion, the crystal chemical nature of these octahedral sheets has been studied on this homoanionic sample.

X-ray powder diffraction patterns (XRD) were recorded on a Philips diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. Unit-cell parameters were refined by a least-squares method from the recorded d-spacings. Infrared (IR) spectra were recorded on a Perkin Elmer 580B spectrophotometer in the range 4000–200  $\text{cm}^{-1}$ . The sample was analyzed using the KBr pellet technique and oriented films on AgCl. The 300–200- $\text{cm}^{-1}$  region was scanned using a CsI crystal. Electron micrographs and electron diffraction patterns were obtained using a Siemens 102 Elmiskop apparatus.

### RESULTS AND DISCUSSION

#### *Electron diffraction and X-ray diffraction data*

Electron micrographs of the Al-Li double hydroxide showed a platy morphology with a distinct hexagonal

<sup>1</sup> On leave from: Centro de Edafología y Biología Aplicada del Cuarto, C.S.I.C. Apto. 1052, Sevilla, Spain.

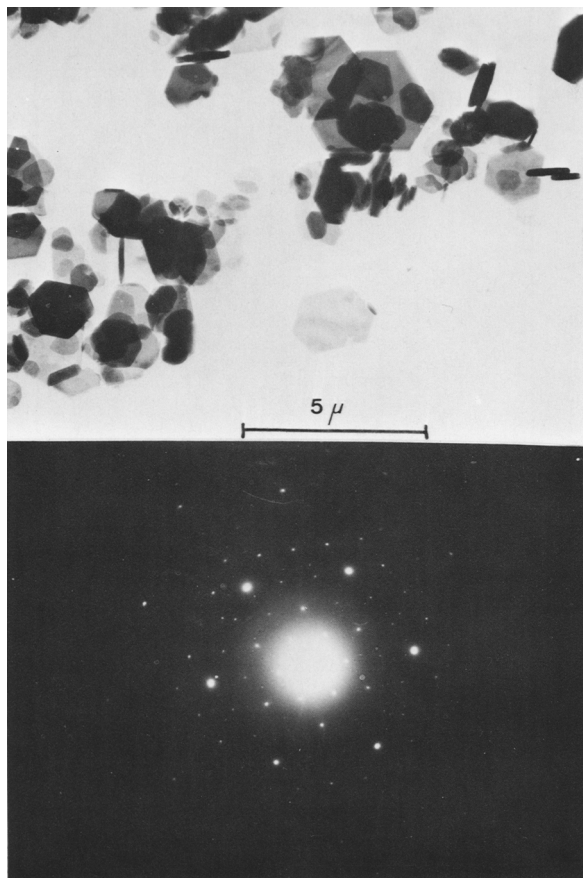


Figure 1. Transmission electron micrographs (TEM) and electron diffraction pattern for  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ . Particle size ranges between 1 and  $2.5 \mu\text{m}$ .

outline (Figure 1a) which resembles that observed for hydroxalite-like compounds (Taylor, 1973).

Selected area electron diffraction (SAD) patterns which correspond to a projection of the structure on its (001) plane exhibit hexagonal symmetry (Figure 1b), and all of the particles studied showed evidence of a superlattice with  $a = 5.32 \text{ \AA}$ . This result suggests ordering of cations among octahedral sheets as described by Taylor (1969). A schematic representation of the octahedral sheet is shown in Figure 2. The Al ions are arranged as in gibbsite, and the vacancies are filled with lithium cations. Anions are present between the sheets to balance the resultant charge. The increase in the  $b$  parameter from gibbsite ( $5.073 \text{ \AA}$ ) to Al-Li double-hydroxide ( $5.32 \text{ \AA}$ ) suggests that the lithium cations remove some of the corrugations present in gibbsite sheets.

SAD patterns of some hydroxalite-like minerals ( $x = 0.25$ ) also show hexagonal symmetry (Taylor, 1973; Bish, 1978b). However, in these materials phase

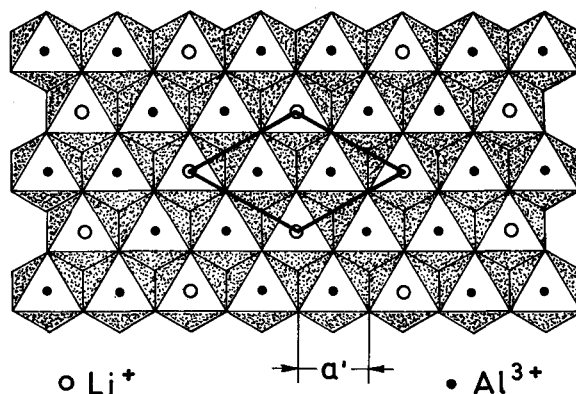


Figure 2. A view of the ordered octahedral sheet in  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$ , showing the unit cell in the (001) plane ( $a = b = \sqrt{3} \cdot a'$ ).

segregation was always present, and some of the particles showed a reflection at  $\sqrt{3} \cdot a'$ , where  $a'$  is the octahedral dimension, which is consistent with ordering of di- and trivalent cations in a 2:1 ratio (Taylor, 1969).

Table 1 shows the XRD data for the Al-Li double hydroxide. Consistent with cation ordering, most of the observed reflections can be interpreted on the basis of a hexagonal supercell with dimensions  $a = 5.32$  and

Table 1. Indexing of powder pattern for  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ .

$d_{\text{obs.}}$ ( $\text{\AA}$ )	Ordered supercell		Random		$I_{\text{obs.}}$
	$d_{\text{calc.}}^1$	$hkl^1$	$d_{\text{calc.}}^2$	$hkl^2$	
7.6	7.62	002	7.62	002	100
4.40	4.41	101			15
4.12					<5
3.96	3.94	102			<5
3.78	3.81	004	3.81	004	90
2.54	2.54	006	2.54	006	20
2.52	2.51	112	2.51	102	40
2.49					
2.27	2.27	201			6
2.25					
2.21	2.21	202	2.21	007	10
		106			
2.11	2.10	203			<5
1.941	2.00	115	2.00	105	<5
1.896	1.905	008	1.905	008	15
1.784	1.761	108			<5
1.692	1.693	009	1.693	009	<5
1.600	1.589	109			<5
1.514	1.512	215	1.524	00,10	<5
1.471	1.470	303	1.470	113	20
1.445	1.447	10,10	1.428	109	15
1.371	1.370	305	1.371	115	5

obs. = observed; calc. = calculated.

<sup>1</sup> Based on a hexagonal cell with  $a = 5.32$  and  $c = 15.24 \text{ \AA}$ .

<sup>2</sup> Based on a hexagonal cell with  $a = 3.07$  and  $c = 15.24 \text{ \AA}$ .

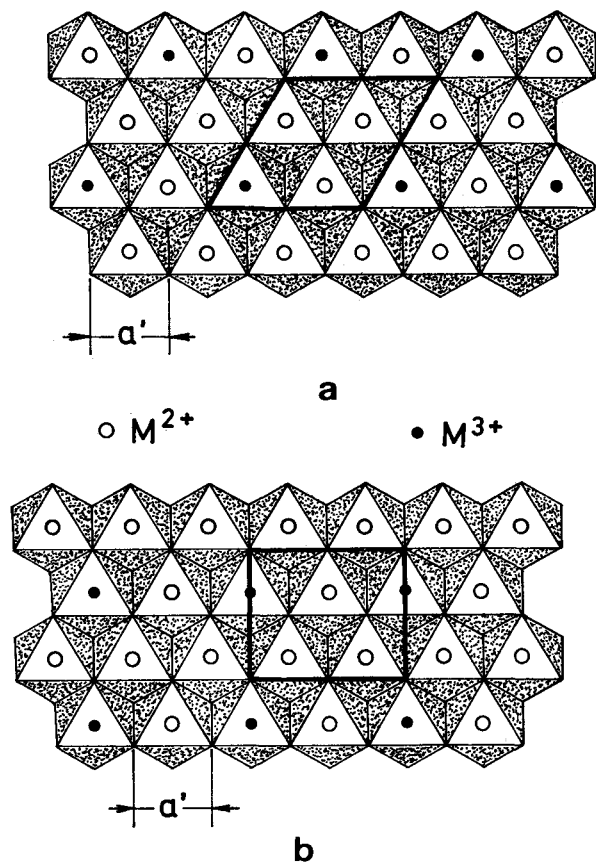


Figure 3. Cation ordering in octahedral sheets for  $M^{2+}/M^{3+} = 3$ : (a) hexagonal supercell with  $a = b = 2a'$ ; (b) orthorhombic supercell with  $a = \sqrt{3} \cdot a'$  and  $b = 2a'$ .

$c = 15.24 \text{ \AA}$ , although a lower symmetry for this type of compounds should not be ruled out (Brindley and Kikkawa, 1979). The only medium intensity reflection whose indexing requires a supercell is at  $4.40 \text{ \AA}$ ; this reflection can be indexed as 101 on the basis of the  $a$  parameter obtained from electron diffraction and the  $c$  parameter calculated from the basal reflections. This reflection may be used as a criterion of cation ordering within the octahedral sheet for hydrotalcite group minerals. Gastuche *et al.* (1967) also showed an XRD peak at  $4.57 \text{ \AA}$  which they interpreted as an indication of some degree of cation ordering in Mg-Al hydroxycarbonates. In their material, the octahedral cation arrangement will be similar to that shown in Figure 2 for the  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$  phase which was previously considered by Brindley and Kikkawa (1979) for a  $M^{2+}/M^{3+}$  ratio of 2. For these ordered layer compounds, the octahedral sheet possesses the maximum charge ( $\sim 25 \text{ \AA}^2/\text{Q}$ ).

No superlattice reflections or related effects, however, have been found for hydrotalcite-like compounds on which detailed structure determinations have been

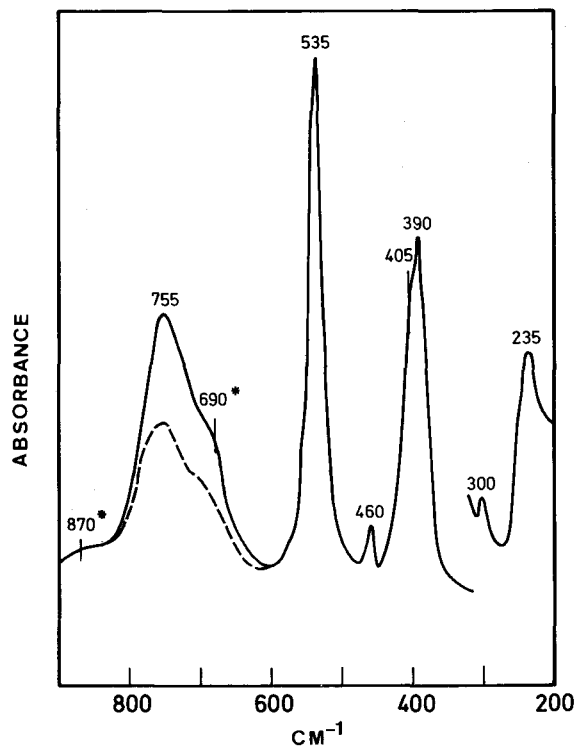


Figure 4. Infrared (IR) spectrum of  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$  from  $900$  to  $200 \text{ cm}^{-1}$ ; solid line = randomly oriented crystals in a KBr disk; dashed line = oriented film with the IR beam perpendicular to the (001) faces (starred peaks are due to  $\text{CO}_3^{2-}/\text{HCO}_3^-$  species).

carried out (Allmann, 1968; Allmann and Jepson, 1969; Ingram and Taylor, 1967). This may be due to the  $M^{2+}/M^{3+} = 3$  ratio of many natural minerals. However, for this ratio, two different ordered arrangements of cations are possible as shown in Figure 3a and 3b, one based on a hexagonal supercell with  $a = 2a'$  (Brindley and Kikkawa, 1979), and the other based on an orthorhombic supercell with  $a = \sqrt{3} \cdot a'$  and  $b = 2a'$ . The charge density in both cells is  $\sim 33 \text{ \AA}^2/\text{Q}$ . However, none of these ordered sheets has been found in either synthetic or natural samples.

#### Infrared analysis

The IR analysis of inorganic solids for which detailed crystal determinations are lacking is usually applied separately for the molecular (internal) and the lattice (external) vibrations. It is generally admitted that the molecular vibrations ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ) are independent of the lattice vibrations of the coordinated groups present in the sheet structure ( $\text{AlO}_6$ ,  $\text{LiO}_6$ ). The IR spectrum of  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$  is shown in Figure 4. Molecular vibrations due to carbonate or bicarbonate anions as well as those due to hydroxyl groups have been considered previously (Serna *et al.*, 1977). Octahedral cat-

Table 2. Normal modes for  $[\text{Al}_2\text{LiO}_6]$  in  $D_{3d}$  symmetry.

	$A_{1g}^R$	$A_{2g}$	$E_g^R$	$A_{1u}$	$A_{2u}^R$	$E_u^R$
Li					1	1
Al		1	1		1	1
O	2	1	3	1	2	3
Total	2	2	4	1	4	5
$T_{\text{acoust.}}$					-1	-1
	2	2	4	1	3	4
$T^R\text{Al}_2\text{LiO}_6 = 3A_{2u} (T_z) + 4E_u (T_x, T_y)$						

R = Raman active; IR = IR active.

ion ordering is indicated in the IR spectrum by the noticeable sharpness of the lattice absorption bands at 755, 535, 460, 405, 390, 300, and 235  $\text{cm}^{-1}$ .

For the study of lattice vibrations it is convenient to consider the translations of the atoms in the anion  $[\text{Al}_2\text{LiO}_6]$  with the ideal  $D_{3d}$  symmetry, i.e., only motions within an ideal octahedral sheet are assumed. In addition, no consideration is given to the actual size and shape of the particles. The predicted lattice vibrations (Table 2) are  $2A_{1g} + 2A_{2g} + 4E_g + A_{1u} + 3A_{2u} + 4E_u$ , from which the last two species are IR active with translations moments along the  $z$  direction ( $A_{2u}$ ) and  $x$ ,  $y$  directions ( $E_u$ ). These octahedral vibrations can be separated into motions of  $\text{AlO}_6$  and  $\text{LiO}_6$ , because vibrational interactions between these groups are weak or negligible (Tarte, 1967). According to Tarte,  $\text{AlO}_6$  vibrations lie between 680 and 400  $\text{cm}^{-1}$ , while vibrations due to  $\text{LiO}_6$  groups have been identified below 300  $\text{cm}^{-1}$ . Consequently, the seven IR active vibrations can be separated as:  $T^R_{\text{Li}} = A_{2u} + E_u$  and  $T^R_{\text{Al}} = 2A_{2u} + 3E_u$ .

Correlations between the molecular group of the octahedron ( $O_h$ ) with the site group of the  $\text{Al}^{3+}$  cation ( $D_3$ ) and the factor group of the sheets ( $D_{3d}$ ) permit the normal modes to be expressed in terms of Al-O stretching and O-Al-O bending vibrations. These results are shown in Table 3, along with the wavenumbers for the lattice vibrations of  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$  with interlayer  $\text{CO}_3^{2-}$  anions.

A complete agreement is obtained between the number of lattice vibrations expected in terms of the  $D_{3d}$  symmetry and that observed for the  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$  cation. The absorption at  $\sim 760 \text{ cm}^{-1}$ , assigned as Al-O stretching, shows different relative intensity for the samples dispersed in KBr pellets and those deposited on AgCl windows (Figure 4). Therefore, this absorption was assigned to the  $A_{2u}$  species (Al-O stretching) in which the transition moment is parallel to the  $z$  direction.

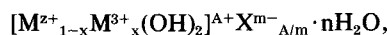
## CONCLUSIONS

$[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$  is a hydrotalcite-like compound, and the general formula given by Taylor (1973)

Table 3. Lattice vibrations and assignments for  $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3\cdot n\text{H}_2\text{O}$ .

Assignments	Wavenumbers ( $\text{cm}^{-1}$ )
Al-O ( $A_{2u}$ )	755
Al-O ( $E_u$ )	535
Al-O ( $E_u$ )	460
O-Al-O ( $E_u$ )	405
O-Al-O ( $A_{2u}$ )	390
Li-O ( $A_{2u}$ )	300
Li-O ( $E_u$ )	235

for such compounds,  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{X}^{m-}_{x/m}\cdot n\text{H}_2\text{O}$ , should be extended to include the monovalent lithium cation as follows:



where  $A = x$  for  $z = 2$  and  $A = 2x - 1$  for  $z = 1$ . The formula applies only to cations in octahedral arrangement. Although there is a general tendency towards cation disorder in these compounds, in the particular material considered here the octahedral sheets are largely ordered. This ordering may arise because any different octahedral arrangement of Al and Li cations is improbable in view of Pauling's rules.

## ACKNOWLEDGMENTS

We thank Dr. J. Serna, of the Physics Department, University of Madrid, for taking the TEM and SAD pictures.

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(Received 26 April 1981; accepted 7 July 1981)

**Резюме**—Слоистая двойная гидроокись с химическим составом  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$ , где  $\text{X}^-$ — межслойный анион, была гидротермически синтезирована при температуре  $30^\circ\text{C}$  из алюминотри-(сек-бутоксид) и литиевого карбоната. Электронные микрографы показали, что продукт реакции имеет пластинчатую морфологию с отличающейся гексагональной симметрией. Это было подтверждено образцами электронной дифракции выбранных мест, соответствующих проекции структуры на (001) плоскость. Получено свидетельство существования сверхсети с  $a = 5,32 \text{ \AA}$ , что указывает на упорядочение катионов в октаэдрических местах. Данные по порошковой рентгеновской дифракции могут быть объяснены также с помощью гексагональной сверхячейки с размерами  $a = 5,32 \text{ \AA}$  и  $c = 15,24 \text{ \AA}$ . Расположение октаэдрических мест кажется быть подобным расположению в гибbsite, но промежуток занят катионами лития. Анионы должны присутствовать между слоями для балансировки заряда. Полное приписание наблюдаемых инфракрасных колебаний сети может быть сделано для аниона  $[\text{Al}_2\text{LiO}_6]$  с идеальной  $D_{3d}$  симметрией, для движений в одном октаэдрическом слое. Результаты показывают, что  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$  является гидроталькоподобным соединением с октаэдрическими катионами в большинстве упорядоченными. Общая формула для гидроталькоподобных соединений  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{X}^{m-}_{x/m}\cdot n\text{H}_2\text{O}$  должна быть расширена так, чтобы включать моновалентный катион лития. [E.C.]

**Resümee**—Ein geschichtetes Doppelhydroxid mit einer chemischen Zusammensetzung  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$ , wobei  $\text{X}^-$  ein Zwischenschicht-Anion ist, wurde hydrothermal bei  $130^\circ\text{C}$  aus Aluminium-tri-(sec-Butoxid) und Lithiumkarbonat synthetisiert. Elektronenmikroskopische Aufnahmen zeigten, daß das Produkt eine plättchenförmige Morphologie mit hexagonaler Symmetrie aufweist, was durch Elektronendiffraktometerdiagramme von bestimmten Bereichen bestätigt wurde, die einer Projektion der Struktur auf die (001) Ebene entsprach. Weiters wurde festgestellt, daß eine Überstruktur mit  $a = 5,32 \text{ \AA}$  vorhanden ist, die auf eine Ordnung der Kationen auf den Oktaederplätzen hindeutet. Auch die Röntgenpulverdiffraktometerergebnisse können im Hinblick auf eine hexagonale Überzelle mit  $a = 5,32 \text{ \AA}$  und  $c = 15,24 \text{ \AA}$  interpretiert werden. Die Anordnung der Oktaederplätze scheint der von Gibbsite zu entsprechen, wobei jedoch die Leerstellen von Lithium-Kationen besetzt sind. Anionen müssen zwischen den Schichten vorhanden sein, um die Ladung auszugleichen. Eine vollständige Bestimmung der beobachteten Infrarot-Gitterschwingungen kann für das Anion  $[\text{Al}_2\text{LiO}_6]$  mit der idealen  $D_{3d}$ -Symmetrie für Schwingungen innerhalb einer Oktaederschicht gegeben werden. Die Ergebnisse zeigen, daß  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$  eine Hydrotalkit-ähnliche Verbindung ist, in der die Oktaeder-Kationen weitgehend geordnet sind. Die allgemeine Formel der Hydrotalkit-ähnlichen Verbindungen  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{X}^{m-}_{x/m}\cdot n\text{H}_2\text{O}$ , sollte so erweitert werden, daß das einwertige Lithium-Kation aufgenommen werden kann. [U.W.]

**Résumé**—Un hydroxide double à couches ayant une composition chimique  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$ , où  $\text{X}^-$  est un anion intercouche a été synthétisé hydrothermalement à  $130^\circ\text{C}$  à partir de carbonate aluminium-tri-(sec-butoxide) et de carbonate lithium. Des micrographes électroniques ont montré que le produit avait une morphologie à plaques avec une symétrie hexagonale distincte, ce qui a été confirmé par des clichés de diffraction électronique correspondant à une projection de la structure sur la face (001). On a obtenu l'évidence d'un super-réseau avec  $a = 5,32 \text{ \AA}$ , indiquant un rangement de cations parmi les sites octaédriques. Les données de diffraction poudrée aux rayons-X peuvent aussi être interprétées par référence à une supermaille ayant les dimensions  $a = 5,32 \text{ \AA}$  et  $c = 15,24 \text{ \AA}$ . Le rangement des sites octaédriques semble être celui de la gibbsite, mais avec les vides remplis de cations de lithium. Les anions doivent être présents entre les feuillets pour balancer la charge. On peut complètement assigner les vibrations du infrarouge observées pour l'anion  $[\text{Al}_2\text{LiO}_6]$  ayant la symétrie idéale  $D_{3d}$  pour des mouvements au sein d'un feuillet octaédral. Les résultats montrent que  $[\text{Al}_2\text{Li}(\text{OH})_6]^+\text{X}^-\cdot n\text{H}_2\text{O}$  est un composé semblable à l'hydrotalcite ayant des cations en grande partie ordonnés. La formule générale pour les composés semblables à l'hydrotalcite  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{X}^{m-}_{x/m}\cdot n\text{H}_2\text{O}$  devrait être élargie de manière à inclure le cation de lithium monovalent. [D. J.]