Layered Double Hydroxides
And the Origins of Life on Earth

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Foreword

The study of the Origins of Life is one that cannot be defined in terms of a single discipline. Any meaningful discussion on the topic is bound to include material from such diverse areas as geology, physics, astronomy, chemistry, biology, and philosophy. This results in the discussion being exceptionally long, even if it uses only general concepts. Therefore, this will not be a meaningful discussion on the problem of the Origins of Life. Rather, the first part of this work is intended as an introduction to the current state of the Origins of Life community and how the research presented in Part II plays a part. The research covered in Part II is original and was performed over the last two years by the author with significant assistance from other group members. A fair amount of detail is included in that section, along with several necessary definitions, presented in a glossary.

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Many thanks must first go to Dr. Paul Braterman, for introducing me to the field of Origins of Life research, and for his role as a mentor, major professor, and friend. Dr. Joseph Bocclair and Faith Yarberrry contributed greatly to this work, collecting and analyzing data, consulting on the work while in progress, and aiding in writing as well. Thanks also go to Jianping Jiang, Shaowei Lou, and Zhiming Wang for contributions to the various publications which form a central part of this work. Finally, I wish to thank the many friends and family who reviewed and critiqued Part I of this work to make it fit for the layman to understand, most especially Riley Stewart, Jessica Tartaro, Elizabeth Brister, Inna Vitol, Prakash Joshi, and Joshua Irish.
Part I

A General Survey of Inorganic Chemistry and the Origins of Life

1. Introduction to the Study of the Origins of Life

In The Beginning...

Theories abound about the Origins of Life. Much like earlier ideas of spontaneous generation in biology, phlogiston in chemistry, and æther in physics, they are put forth as the best answers given the available information. Often they are simply guesses at possible life-forming events. Some are advocated doggedly by prominent scientists and popular media sources; others are looked on as interesting possibilities only. There seem to be almost as many theories as there are research groups working in the field. None to date has proven to be satisfactory to the vast majority, although some have held the popular consensus for a time. Large gaps exist between one group’s area of research and another’s. Thus, it is currently impossible to put forth a “complete” theory on the origins of life; we simply don’t know enough to even begin guessing at all the necessary components and processes that would need to happen for life to arise. However, this has not stopped some from trying. In this paper, we shall confine ourselves to three of the most popular theories on the subject.

Things to consider when proposing a theory

As mentioned earlier, the question of why we are here and how we got here requires input from very diverse sources. Astronomy, physics, chemistry, geology, and biology are the most important for our purposes, although other disciplines may also play significant parts. This requirement stems from a property of the question; how we got here depends on what things were like before life originated. More specifically, how we got here depends on what almost everything was like before life originated. We must therefore consider the conditions not only on the early Earth, but in the primordial solar
system, the Milky Way, and even events that transpired shortly after the creation of the universe in the Big Bang. Unfortunately, direct observation of the early Earth’s conditions is impossible. Instead, we must rely on the scant evidence that remains today. After over 4.5 billion years of cosmological, geological, and biological activity, there is very little of this evidence left to be found. Fortunately, some rocks from ~4 billion years ago still exist. In some cases, the “rocks” in question are no more than crystals. Tiny zircons have traveled from the molten bowels of the Earth to the surface, then been pulled back in, and finally thrown out again, surviving unchanged because of their special stability once formed. The other “rocks” have often been changed by metamorphic processes. This means that much of the evidence we could have found from these rocks has been destroyed by the intense heat and pressures that change rock from one form to another. Some slightly younger rocks (~3.6 billion years old) still exist as the original sediments; by this time, however, evidence of life already exists. Additional information can be gleaned from studying the surfaces of Mars and the moon, which have remained relatively unchanged through the eons except for the occasional impact. Thanks to the Apollo missions in the late 1960s and early 1970s, we have some actual samples of lunar rocks to study. True samples of martian rock are rare. Impacts on Mars occasionally send fragments of its surface hurling into space; sometimes a piece floats towards Earth, where it is pulled in by gravity.

Other evidence may come from space. It has become increasingly apparent that the conditions on the early Earth were very dependent on the conditions in the early Solar System, which in turn is dependent on galactic conditions at the time. Some research groups are searching the upper atmosphere for tiny interplanetary dust particles that may hold clues to the conditions of the primordial Solar System. Others are looking further out into space, into the interstellar medium, searching for clues on how some of the first all-important organic molecules may have been formed. Still others examine far away stars and their planetary systems in an attempt to understand how our Solar System formed.

The goal of a “complete” theory of the origins of life is, quite simply, to put forth a reasonable idea of how life first arose. “Life” in this case means anything that is
capable of growth, replication, and of spreading to other environments. As we will see, there are several different ways this condition can be met.

2. Conditions on the early Earth

Most theories about the conditions in which life arose involve some description of the early Earth’s atmosphere. This was a topic of debate long before A. I. Oparin wrote his classic work of origins of life research literature, *The Origin of Life*. Oparin (and others) reasoned that in order for proteins and nucleic acids to be synthesized, an environment was required where electrons and hydrogen could be freely available. This environment needed to have high concentrations of ammonia, methane, and H$_2$, the simplest forms of nitrogen, carbon, and hydrogen that met the requirement. Thus, the atmosphere of the early Earth must have had these compounds floating about in it at a reasonably high concentration. Later, evidence to support this claim would come from the famous Urey-Miller experiment in 1953. However, there is no evidence from the geologic record to support these claims of a “reducing” atmosphere. On the contrary, many scientists have found reason to believe that the early atmosphere was fairly neutral, with little or no available electrons and very little free oxygen (oxygen as O$_2$) present. This will be discussed later.

Another important consideration is the composition of the early Earth’s oceans. Fossil records strongly suggest that life evolved in water and then adapted itself to land. It seems reasonable to assume that life must have therefore *arisen* in (or near) the oceans as well. The problem is that the ocean does not bother to keep a record of its composition over time. Thus, we resort to the geologic record again; any sediment laid down 4 billion years ago would almost certainly have been deposited by an early ocean. Certain isotopic ratios suggest that the temperature of the oceans was much higher than it is today, somewhere around 50–90 °C. The existence of certain amounts of CO$_2$, H$_2$O, and other “volatile” compounds in these rocks indicate the presence of an ocean–air carbon dioxide–carbonate–bicarbonate buffer:

$$\text{CO}_2(g) = [\text{HCO}_3^-]_{(aq)} = [\text{CO}_3^{2-}]_{(aq)}$$
This sort of complex buffer chemistry would have acted as a pH buffer in the early oceans, maintaining a pH range between 7-8, with some extreme areas (e.g. near intense heat or geologic activity such as an undersea volcano) around pH 10. Any organic compounds that took part in the first life-forming event would have had to exist in this environment for at least a short time. This, of course, would affect how the first organisms were created. Unfortunately, fossil records have yet to divulge the chemical makeup of the first organisms, and it is quite possible that this information no longer exists on Earth.

The situation on the early Earth is further complicated by the state of affairs in the early solar system. Before about 4.5 billion years ago, the planets were still forming. Although most of the debris in the solar system had been collected by this time, it is believed that there were still many large planetessimals floating about, mini-planets on rogue trajectories that could smash into a planet and produce enough heat to melt the entire crust. This period in Earth’s history, where the planet itself was formed and thinly crusted but still frequently hit by large meteors, is called the Late Heavy Bombardment. Geologic data from the Moon suggests that it was formed during this time by a Mars-sized object hitting the Earth with considerable force. Imagine two soft pieces of clay floating in space, with one piece about 1½ times as large as the other. If the smaller piece were fired at its larger sibling with enough force, so that it struck a glancing blow, it would tear into the clay and pull off a chunk from the outer portion. The fired clay would then proceed off on a newly altered path and end up someplace else. Both pieces would be very deformed by this, but the larger piece would now have a portion of itself orbiting around it. During the Late Heavy Bombardment, the moon-former did something similar to this on a grander scale. Since large molten bodies of rock still have gravity, any non-spherical deformations would be drawn back towards their respective centers. The Earth’s gravity was apparently stronger than its newfound satellite’s inertia, and our present heavenly body is the result.

Obviously, sending the entire mass of the Earth into a liquid state kills any living Carbon-based life immediately, and most likely pyrolizes (literally, “breaks by fire”) any organic compounds laying around as well, reforming Carbon Dioxide (CO₂) and perhaps some Methane (CH₄). Depending on the rarity of life-forming events, this may only delay
the inevitable; on the other hand, it may also leave the planet permanently sterile. This “impact frustration” of the origins of life plays another part as well: global sterilization events determine the earliest possible times for life-forming events. Life can only originate after the last sterilization takes place. For the early Earth, this could mean the end of the Late Heavy Bombardment, some 4.1 billion years ago. However, evidence of life is documented in rocks 3.8 billion years old; this means that the window for life’s origins is narrowed to about 300-500 Myr (1 Myr = 1 million years). In this amount of time, the earliest biomolecules need to have been synthesized. A constant source of energy must have been found and the components of some information carrying and transfer system must have been built. All of this must have been done in an environment capable of allowing growth and reproduction. Finally, the first forms of life must have begun to adapt to changes in their surroundings and to spread (however slowly) into other environments. By 3.6 Gyr (3.6 billion years) ago, organisms must have been diverse enough to have shaped themselves to look like modern cyanobacteria (blue-green algae). Thus, any theory put forth on the Origins of Life must consider a very diverse set of factors, manage somehow to accomplish the first basic life processes “from scratch”, and do it within the time span of 300-500 million years.

3. Current Theories on Abiogenesis (The Origin of Life)

“Soup Theory”

Perhaps the most famous theory on the origins of life is the idea of a ‘primordial soup’ from which life arose. The process is simple: primitive carbon-containing molecules began to react, using some constant energy source such as geothermal heating or light from the Sun, and formed more complex organic molecules. The constant input of energy allowed the reactions to drive towards ever-increasingly complex molecules. This process continued until amino acids (for making proteins), sugars (for DNA/RNA), and lipids (for membranes) formed themselves into a single, concerted set of reactions, capable of using an energy source to drive the growth of the overall system. Thus, the first organism was formed. It seems straightforward enough.
However, there are a number of problems questions that this theory fails to explain, and some phenomena that seem to contradict it altogether. What reaction conditions were involved with making the first organic molecules? What was the driving force for making more complex molecules? What possible forces would have caused these reactions to form self-supporting systems? Many attempts have been made to answer these and other questions in a manner consistent with this theory. Doubtlessly, the most famous example of this is the Urey-Miller experiment.

In 1952, Stanley Miller (then a graduate student in Harold Urey’s research group) proposed a relatively simple experiment: what if primordial lightning was enough to synthesize the necessary prebiotic soup? To answer this, Miller constructed the device shown in Figure 1. At the bottom is a container of water to simulate an early ocean. The larger vessel at the top is meant to contain the mixture of gases that simulates the early Earth’s atmosphere. The tubing connecting the two vessels allows the gases and any water vapor from the ‘ocean’ to circulate through the apparatus. Finally, two electrodes are inserted into the upper vessel and used to create a spark to simulate lightning, while the lower vessel was heated to produce the necessary water vapor and circulate the gases.

The results were far more exciting than expected. Table 1 shows a brief assay of the compounds identified from the experiment. Approximately 15% of the Carbon in the system (originally as methane, CH₄) was converted into organic compounds. The most abundant of these was Formic acid, a compound which can be used to make sugars. More importantly, 2.1% of the total carbon was converted into Glycine, an amino acid that is found universally in all known life. Another amino acid, Alanine, was also formed in 1.7% yield. To many, this strongly implied that the early Earth would have made any necessary organics in this way, and that life was a natural (if not inevitable) consequence of this sort of chemistry. By 1953, it seemed, the problem of the origins of life on Earth had been solved. Further experiments were necessary only to fill in the details.

‘The details’ eventually proved to be very difficult to reconcile with the original theory. As geologists began to analyze the oldest known rock samples, they found that most of the minerals formed could not have done so in the proposed atmosphere used in Miller’s model. In fact, the rocks could only have formed, it seemed, in a neutral atmosphere, where no molecular Hydrogen (as H₂) or Oxygen (as O₂) was present. Other
implications came from astronomers studying the formation of the Solar System: if the early Earth formed the way they thought it did, then the 'reducing' atmosphere so essential to the Urey-Miller experiments could never have existed. This cast the entire scenario into doubt, until later experiments by Miller and others (most notably Cyril Ponnamperuma) showed that the much-needed organics could still be synthesized via primordial lightning, but in lower yields and after a much longer time period. To this day, the Miller research group in San Diego is still performing spark-discharge experiments in an effort to prove this theory.

**Figure 1.**
Schematic representation of the Urey-Miller apparatus.
Table 1. Yields from Sparking a Mixture of CH$_4$, NH$_3$, H$_2$O, and H$_2$. The Percentage Yields Are Based on Carbon (59 mmoles (710 mg) of Carbon Was Added as CH$_4$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmoles</td>
</tr>
<tr>
<td>Glycine</td>
<td>630</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>560</td>
</tr>
<tr>
<td>Sarcosine</td>
<td>50</td>
</tr>
<tr>
<td>Alanine</td>
<td>340</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>310</td>
</tr>
<tr>
<td>N-Methylalanine</td>
<td>10</td>
</tr>
<tr>
<td>α-Amino-n-butyric acid</td>
<td>50</td>
</tr>
<tr>
<td>α-Aminoisobutyric acid</td>
<td>1</td>
</tr>
<tr>
<td>α-Hydroxybutyric acid</td>
<td>50</td>
</tr>
<tr>
<td>β-Alanine</td>
<td>150</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>40</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>4</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>6</td>
</tr>
<tr>
<td>Iminodiacetic acid</td>
<td>55</td>
</tr>
<tr>
<td>Iminoacetic-propionic acid</td>
<td>15</td>
</tr>
<tr>
<td>Formic acid</td>
<td>2330</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>150</td>
</tr>
<tr>
<td>Propionic acid</td>
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<tr>
<td>Urea</td>
<td>20</td>
</tr>
<tr>
<td>N-Methyl urea</td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>
Another theory uses inorganic materials help synthesize the all-important prebiotic molecules. Put forth by Bernal in 1951, the ‘weak role’ theory uses clays and other minerals as early sources of order. In an otherwise chaotic solution of simple inorganic carbon compounds such as carbonate or urea, certain minerals (such as hydroxyapatite or montmorillonite) could catalyze the formation of larger, more complex organic molecules such as amino acids and nucleic acids. Further catalysis could lead to the production of chains of these compounds, eventually forming proteins and genetic information carriers. The only source of information in this system would come from the lattice structures of the minerals themselves, but the reactions catalyzed would vary from mineral to mineral. Many different mineral types might have been needed to carry out the synthesis of all the early biomolecules. Depending on the type of material involved and its crystal structure, chiral compounds could be formed in this way. Still other minerals could have trapped these early organic molecules from solution and stored them, concentrating them in an environment where further reactions could occur. Eventually, the organics would find their way back into solution (but not necessarily into the ocean proper) and begin to form systems of reactions with other molecules, taking in compounds from one source and making more complex molecules from them.

A logical implication of Bernal’s theory is that these processes would continue until either the source compounds were depleted or the system built up a so many products that other reactions become dominant. Aided by the continued presence of the mineral catalysts, the systems could start producing the first biological compounds, such as RNA and protein. Some of these new products might begin to catalyze their own production, leading to an exponential buildup of RNA and protein-like compounds. Eventually some sort of encapsulation would occur, allowing for a greater concentration of various products inside these first primitive ‘cells’. Those ‘cells’ with proteins or other large molecules stuck in their membranes would be capable of bringing in fresh source compounds and of removing byproducts; all others would simply cease to function after a relatively brief period of time. The first organisms would then form
when some of these systems managed to successfully break apart and continue to function.

The Bernal theory has become an integral part of the “RNA World” theory, which postulates that life began after some form of catalytic RNA molecules began appearing in large concentrations. To many, the need for these reactions to occur in solution fits in well with the idea of a “prebiotic soup”; the reducing conditions necessary for Urey-Miller-type syntheses could come from mineral catalysis of compounds in the early Earth’s atmosphere or dissolved in the early ocean. Astronomy has contributed the idea that many of the necessary prebiotic molecules could have been synthesized in space. Many observed molecular clouds have large amounts of methane, ammonia (NH₃), and molecular Hydrogen in them. Reactions in mixtures of these gases have produced a wide range of products; the compounds detected to date strongly suggest that molecules such as glycine should also be present. For various reasons, however, glycine is extremely difficult to detect and no satisfactory method has been found to identify the compound in molecular clouds. Nonetheless, the possibility of having prebiotic synthesis occur in space and the products delivered to the early Earth presents an alternative form of “primordial soup” for us to consider. This is an area of active research in the Origins of Life community.

_Grahm Cairns-Smith’s Inorganic Ancestor_

Around 1980, an English scientist by the name of Grahm Cairns-Smith proposed a very interesting theory. Life may not necessarily have begun based on carbon chemistry; it could have instead arisen in the form of mineral surface-catalyzed processes. These minerals could have contained information in highly redundant crystal lattices, and achieved change (evolution) by spontaneous variations in lattice structure. Reproduction could be achieved by catalyzing more mineral-forming processes. To spread from one environment to the next, Cairns-Smith proposed that the minerals be of a lumpy, runny consistency, thus capable of having pieces of themselves slough off from time to time, to be carried down a stream and settle in somewhere else. According to this theory, these minerals would have been the first to catalyze protein syntheses, and
eventually, to make RNA and DNA. At this point, this new material could begin to carry information about its own replication, as well as the production of new proteins. The proteins would catalyze other processes, such as the breakdown of widely available molecules as food sources and the production of hydrophobic (‘water-hating’) molecules. These molecules would eventually enclose the DNA-RNA-protein systems to form the first cells.

This “genetic takeover”, as Cairns-Smith calls it, forms the basis of the current ‘strong role’ theory of life’s inorganic ancestry. These first organisms would have had to arise without the benefits of natural selection, and thus would have changed only because of random “mutations” in their lattice structures. In this case, a consistent lack of change would be preferred to a constantly changing system. Our current biology exists because only minor changes occur at any given point, allowing evidence of some last common ancestor to all modern life to persist as commonalities in every known organism (e.g. ribosomes and a DNA-RNA-protein structured system). Some suggest that, eventually, the clays might have begun to use organic molecules in their own construction, allowing even greater variability in lattice structure. Metal chelating (from Greek kelos=“claw”) agents could have preferentially allowed certain metals to stay in solution while others formed the initial latticework. When the concentration of the chelated metals in solution became high enough, those metals could have begun forming a second, different layer on top of the original lattice. In this manner, the newly forming minerals could have a structure complicated enough to store information and also be able to catalyze the formation of other organic compounds, such as amino acids or nucleic acids. As time progressed, these systems would have faced the same problems that any organisms face: their source of energy would become depleted, and only those that found an alternate energy source would ‘survive’. The rest would simply stop functioning, having no more raw materials to catalyze.

The idea of self-replicating clays is a very interesting one, since very few of the rules from modern biology can have effect. Since the systems are not based on carbon chemistry (at least not at first), the need for a “soup” of some kind is removed. The clays would only need relatively small amounts of water around to form, preferably in a slow-moving stream so that enough of the needed materials could accumulate locally but still
allow for parts of the clays to spread to other areas. The process of replication could occur without the need for catalyzed reactions; a “templating” mechanism could be used, where progressive layers of material form on top of an existing structure. When the lattice becomes large enough, a large piece would break off and be taken downstream a short distance, where it would settle in and begin replication again. The effects of natural selection would occur over a much longer period of time, ranging from a few million to hundreds of millions of years, since the mineral processes occur at much slower rates than organic syntheses do. Because of this, added functionality (such as catalyzing formation of RNA or proteins) would not carry a competition penalty, since any organic products could easily move off into solution before a mineral component would attach to the lattice. Presumably, the advent of photosynthesis by carbon-based life would have obliterated most evidence of these self-replicating clays, by bringing molecular Oxygen into the atmosphere in large amounts. Since these clays are not entirely solid, oxidation would occur throughout the lattices, and the clays would break up into particles and be carried downstream.
Layered double hydroxides (LDH) are anion-exchanging materials that can concentrate, protect, and activate simple organic anionic species of possible relevance to the earliest organisms. They are formed in nature by the weathering of basalts\textsuperscript{1,2} or by precipitation from saline lakes\textsuperscript{1}. They have the general formula $\text{M(II)}_x\text{M(III)}(\text{OH})_{2x+2}\text{Y}$, where, in present-day minerals, M(III) is most commonly Fe or Al, and M(II) is most commonly magnesium (often with partial inclusion of Mn and/or Fe). Nowadays, the anion Y may be $\frac{1}{2}\text{CO}_3$, Cl, or $\frac{1}{2}\text{SO}_4$, although this last may not have been available on the early Earth. The schematic structure is shown in Figure 1; each metal ion surrounded by six hydroxides, and each hydroxide by three metal ions, while the interlayer anion Y (and interlayer water) occupy space between the close-packed metal hydroxide layers. Note that interlayer hydroxide has no free lone pairs, so that it cannot function as a base without disrupting the lattice. Despite this, LDHs are known to act as basic catalysts (see for example Pinnavaia et al., 1995), perhaps because of incorporation of hydroxide or carbonate into the interlayer space. This OH group does, however, have a pendant hydrogen, which can take part in H-bonding to interlayer water, thus enhancing its acidity. LDHs provide a specific, orderly, strongly hydrogen-bonding environment and can readily be prepared in the laboratory, with the prospect of controlling their behavior by varying the layer charge density, the identity of M(II), M(III), Y, the particle size and degree of structural perfection and ordering, and whether reaction occurs on external surfaces or the interlayer space. They are an increasingly important class of materials\textsuperscript{3-4} with applications ranging from environmental clean-up agents\textsuperscript{5-6} to catalysts and catalyst supports.\textsuperscript{3-4,7,15} In the area of catalyst supports much attention has been paid recently to incorporating catalytically important metals such as platinum,\textsuperscript{7} palladium,\textsuperscript{7} and ruthenium.\textsuperscript{8} Many of the preparations concerning LDHs and
these catalyst metals have concerned incorporating the metal in question into the cation layer or adsorbing a metal anion onto the surface of the LDH.

Both strong and weak roles have been suggested for inorganics in the origins of life. According to Bernal’s weak role theory, inorganics may have functioned as a source of order, through concentration and catalysis, without necessarily using anything more sophisticated than the highly redundant information of their lattice structures. According to the strong role theory of Cairns-Smith, Darwinian evolution began with the selective elaboration of information embodied in the lattice variations of inorganic materials, with subsequent genetic takeover by organics. The strong role theory requires that inorganics should also be able to meet the requirements of the weak role theory, but not necessarily vice versa. It is therefore important, without at this stage
attempting to distinguish between strong and weak roles, to establish whether inorganic materials can indeed play the required role of directing reactions of simple precursors towards the formation of more interesting materials.

Which inorganics should be selected for study, out of the enormous number available? Model materials (i.e. those whose behavior can give us insight into the processes leading to the origins of life) would have the ability to concentrate prebiotics of interest, most of which are anionic or polar, and hydrogen-bonding. Candidate materials (i.e. those that, as a matter of historical fact, may have actually played a part in these processes) would in addition have been readily available on the early Earth. For these reasons, we and others have concentrated our attentions on the layered double hydroxides (LDH). These materials have been reviewed in the context of the origins of life by Kuma et al., and more generally by several authors.4,9,19

How the experiments took place

Step 1: Synthesis of Parent Compounds

Every LDH system studied required that the anion of interest be intercalated into a pre-existing LDH latticework. In most cases a LDH Chloride was used; however, a few of the LDH Ni(CN)₄ and Co(CN)₆ compounds were made from a LDH Nitrate (NO₃) parent. Both compounds have similar syntheses, starting from AlCl₃•6H₂O, MgCl₂•6H₂O, NaCl, and NaOH for the LDH Chloride systems, and from Al(NO₃)₃•9H₂O, Mg(NO₃)₂•6H₂O, NaNO₃, and NaOH for the LDH Nitrate systems. Hydrated metal salts (A. C. S. reagent grade) and NaCl were used as supplied by Aldrich, J.T. Baker, Mallinkrodt, and Fisher. Potassium metal-cyanide salts were obtained from the same sources except in the case of K₂Ni(CN)₄, which was synthesized from Ni(CN)₂ and KCN as provided by Alpha Aesar. All water used in these experiments was ultra-pure (18.2 MΩ/cm), obtained from a Millipore Milli Q Plus water purification system.

The procedure for synthesis is dependent upon what ratio of magnesium to aluminum is required for the parent LDH. Usually this ratio was 2:1 Mg:Al; however, ratios of 3:1, 3½:1, and 4:1 were also used when characterizing the interlayer
environment. The desired mass of LDH parent is then used to calculate the relative masses of compounds needed, adding one mole of MgCl or Mg(NO₃)₂ that is required by the system for a buffer. For example, if a 2:1 Mg:Al ratio is needed for a LDH•Cl⁻ parent, 3 moles of MgCl₂·6H₂O is used with 1 mole of AlCl₃·6H₂O. The required masses of metal salts, plus 1 equivalent of sodium salt to bring the total anion concentration to 1 M, are measured and added to a 3-necked round-bottom flask. The solids are then dissolved in about half of the total amount of water to be used and left to stir under a blanket of UHP N₂ gas while the required amount of 50% NaOH (w/w as supplied by VWR) solution is measured. This 50% solution is poured into an addition funnel, along with the remainder of the water required to make the solution 0.1 M in LDH. The entire apparatus is flushed through with UHP N₂ for 15 minutes, and the diluted NaOH solution is slowly titrated into the salt solution. Once the titration is finished, the LDH suspension is refluxed under the N₂ blanket overnight. The suspension is centrifuged to collect the product, then washed with water and re-collected by centrifuging. This washing method is performed 2 more times to remove excess metal salts. All further experiments are conducted under a UHP N₂ blanket or an Ar inert atmosphere.

**Step 2: Synthesis of Systems studied**

Exchange of the LDH parent ion for the anion of interest was straightforward; a moderate amount of LDH parent was exposed to a 0.1M solution of the anion of interest for more than 2 hours. Most often, the suspensions were left to stir overnight (18 to 24 hours). The newly intercalated LDHs (termed LDH hosts) were then collected and washed in the same manner as the LDH parents. This process worked well for all of the metal-cyanide complexes studied. This technique was used to create 2:1 and 3:1 Mg:Al LDH systems with intercalated [Ni(CN)₄]²⁻, [Co(CN)₆]³⁻, [Ru(CN)₆]⁴⁺, [Pd(CN)₄]²⁻, and [Pt(CN)₆]²⁻. The LDH parent was also exposed to 0.1 M [Pt(CN)₆]²⁻ as well, but no measurable intercalation occurred. The LDH CN⁻ systems were made by exposure to CN⁻ concentrations from 0.05–4 M for varying lengths of time, ranging from overnight to two weeks. Noticeable color changes occurred after overnight exposure.
Step 3: Gathering Data

The systems were analyzed using a variety of methods: FT-IR spectroscopy, powder XRD, ICP, HPLC, UV-VIS, C-H-N analysis, and thermogravimetric analysis. The infrared spectra were obtained with a Perkin-Elmer 1760X FT-IR, using a computer interface to gather and process the data. Conventional (non-oriented) spectra were obtained using KBr discs containing approximately 1% sample. Oriented spectra were obtained by placing a drop of dilute aqueous suspension of the material on the horizontal top surface of a barium fluoride disc and allowing the water to evaporate slowly, normally inside a sealed dessicator. The disc was then mounted perpendicular to the sample beam. The XRD traces were gathered using either a Siemens D-500 Diffractometer or a Scintag XDS 2000, both using Cu Kα radiation sources. All powder XRD samples contained approximately 5% CaF$_2$ as an internal standard. Carbon, hydrogen, and nitrogen content were analyzed by Atlantic Microlabs, Inc. HPLC data were acquired with a Waters 501 pump connected to a Waters 996 photodiode array detector collecting from 210 to 400 nm. The HPLC column used was a Phenomenex Columbus 5µ C18 100Å and the mobile phase was an equal mixture of methanol and water, buffered at a pH of 6.5 by a 20 mM phosphate buffer. UV-VIS spectra were obtained either from the HPLC apparatus or from a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Thermogravimetric analysis was performed using a Perkin-Elmer TGA-7 instrument to a maximum temperature of 1,000 °C at a rate of 20.0 °C/min under a nitrogen atmosphere. Data for the metal ratios was gathered using a Perkin-Elmer 5500 ICP/AES. Samples were digested with an equal mixture of 5% nitric and 5% hydrochloric acids; standard metal solutions (used to calibrate the device) were purchased from Aldrich and Alfa Äesar. Standards for magnesium and aluminum were mixed together to allow simultaneous determination of Mg and Al content in the LDHs. ICP data for the anion metals was gathered in separate runs. We performed an average of nine determinations for each metal in each material.
From “Layer-Anion Interactions in magnesium aluminum layered double hydroxides intercalated with cobalticyanide and nitroprusside” published in Chemistry of Materials vol. 11, number 8, pages 2199-2204. Collaborative effort with Paul S. Braterman, Joseph W. Boclair, and Faith Yarberry. Layered materials containing the cobalticyanide \([\text{Co(CN)}_6]^{3-}\) anion were prepared and analyzed via infrared spectroscopy by the author; X-Ray diffraction and ICP analysis were performed by the co-authors.

Abstract

The interactions of cobalticyanide with magnesium aluminum layered double hydroxide are investigated using oriented infrared spectroscopy together with powder X-ray diffraction. Cobalticyanide is known to intercalate into layered double hydroxides in the same manner as ferrocyanide, with its three-fold rotational axis perpendicular to the cation sheets. The intercalated cobalticyanide anion shows a small yet observable deviation from local \(O_h\) symmetry causing small differences between its oriented and non-oriented infrared spectra. Nitroprusside is shown to intercalate into 2:1 Mg:Al LDH with decomposition to form intercalated ferrocyanide and nitrosyl groups of an unidentified nature.

Introduction

LDHs containing transition metals via intercalated metal complex anions, such as ferrocyanide\(^{21-28}\) and cobalticyanide,\(^{29}\) have drawn interest as catalysts,\(^{26}\) mixed oxide precursors,\(^{21-22}\) and in modified electrode formation.\(^{25}\)

While powder XRD is the most usual method of study for these materials, IR spectroscopy has been used to confirm the presence of such anions as sulfate, ferricyanide, and ferrocyanide (Reference 3 and references therein). We have developed a simple technique for obtaining oriented IR spectra for LDH\(^{30}\) and now report the use of this technique to demonstrate slight deformation of the cobalticyanide force field from local \(O_h\) symmetry upon intercalation into LDH.
Experimental

Potassium cobalticyanide \([K_3Co(CN)_6]\) (reagent grade) was used as supplied by Aldrich. For preparing the \([Co(CN)_6]_3\) compounds, a sample of the Mg/Al-LDH chloride (approximately 0.75g LDH, 3.04 meq) was exposed to a solution containing excess potassium salt of the appropriate anion (approximately 50mL of a solution 0.1M in the anion in question). Following the reaction period, the resulting solid is collected and washed repeatedly via centrifuge. All exchange vessels and subsequent products were protected from light in order to prevent photolysis of the anions and/or the exchange products.

Results and Discussion

The insertion of cyanide-containing anions into LDH is very easily demonstrated by the appearance of the v(CN) vibration in the 2200-2000 cm\(^{-1}\) region of the infrared spectrum of the material. Figure 2 shows the infrared spectra (non-oriented) of chloride-, cobalticyanide-, and nitroprusside-containing 2:1 Mg:Al LDHs. The associated data for the LDHs are listed in Table 1. Table 2 compares infrared data for LDH v(CN) and v(NO) with data for the aqueous anions and the potassium (or sodium for nitroprusside) salts. Hansen and Koch reported that the infrared spectra of intercalated and aqueous ferrocyanide were very similar.\(^23\) Likewise the IR data of cobalticyanide reported here are indeed virtually identical in aqueous and intercalated environments showing v(CN) values of 2128 cm\(^{-1}\) and 2127 cm\(^{-1}\) for the intercalated and aqueous species respectively.\(^1\) However, close inspection of the intercalated sample shows a slight broadening of the v(CN) peak (Figure 3), associated with a slight splitting clearly detectable in the full-size spectra prinout.\(^3\) The oriented infrared spectrum of intercalated cobalticyanide is also shown in Figure 2. This v(CN) of the oriented sample is broadly similar to that of the nonoriented sample, showing an absorbance maximum at 2133 cm\(^{-1}\), but with loss of the lower frequency component.
Figure 2. Infrared spectra (nonoriented) of (a) 2:1 Mg:Al LDH chloride, (b) 2:1 Mg:Al LDH cobalticyanide, and (c) 2:1 Mg:Al LDH nitroprusside.

Table 1. Observed Infrared Frequencies (Nonoriented) for 2:1 Mg:Al Containing Chloride, Cobalticyanide, and Nitroprusside (cm⁻¹). Literature values given in parentheses.

<table>
<thead>
<tr>
<th>Anion</th>
<th>ν(OH)</th>
<th>δ(OH)</th>
<th>ν,δ(anion)</th>
<th>lattice vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>3546, 3467</td>
<td>1631</td>
<td></td>
<td>672, 447</td>
</tr>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>3428</td>
<td>1619</td>
<td>2128</td>
<td>677, 449</td>
</tr>
<tr>
<td>[Fe(CN)₅(NO)]²⁻</td>
<td>3465</td>
<td>1636</td>
<td>2143, 2037, 1936 (2143, 2040, 1940)²⁴</td>
<td>660, 448</td>
</tr>
</tbody>
</table>

Table 2. Observed IR Frequencies of Octahedral Cyanide-Containing Anions in Differing Environments. Literature values given in parentheses.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Intercalated</th>
<th>Solid Salt (cation)</th>
<th>Aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>2128</td>
<td>2129 <a href="2128">K</a>²²</td>
<td>2127 (2127)²²</td>
</tr>
<tr>
<td>[Fe(CN)₅(NO)]²⁻</td>
<td>2143, 2037, 1935</td>
<td>2174, 2159, 2144, 1940 [Na]</td>
<td>2142, 1936 (2142)³⁴</td>
</tr>
</tbody>
</table>
Figure 3. Expanded infrared spectra of Mg:Al LDH cobalticyanide a) non-oriented b) oriented (cm$^{-1}$).

Figure 4. Expanded infrared spectra of product from attempted preparation of 2:1 Mg:Al LDH nitroprusside a) non-oriented b) oriented (cm$^{-1}$).
The IR spectrum of nitroprusside (Figure 2) also shows some features that are highly similar in aqueous and intercalated environments (2142, 1936 and 2143, 1935 cm\(^{-1}\), respectively). There are, however, some significant differences: the appearance of a split band with maximum absorbance at 2037 cm\(^{-1}\) in the Mg:Al LDH nitroprusside, and a noticeable splitting of the \(\nu(\text{NO})\) band. We attribute the 2037 cm\(^{-1}\) band, completely absent in both the aqueous and solid sodium salt spectra, to intercalated ferrocyanide, generated by decomposition of the nitroprusside following insertion into the layers. We attribute the splitting of the \(\nu(\text{NO})\) peak to the generation of nitrosyl groups of unknown structure, a byproduct of the nitroprusside to ferrocyanide decomposition. The oriented IR spectrum of Mg:Al LDH nitroprusside, shown in Figure 4, exhibits significant differences from the nonoriented spectrum. Specifically, the oriented spectrum in the \(\nu(\text{CN})\) region shows a suppression of the 2037 cm\(^{-1}\) maximum with a symmetric peak centered at 2045 cm\(^{-1}\) remaining as well as a complete resolution of the two \(\nu(\text{NO})\) peaks, with enhancement of the higher frequency absorption relative to the one at lower frequency.

Reported interlayer spacings show that ferrocyanide,\(^{27}\) ferrocyanide,\(^{26}\) nitroprusside,\(^{19}\) and coalticyanide\(^{29}\) all orient themselves in a LDH interlayer with their 3-fold rotational axis perpendicular to the hydroxyl sheets. Table 3 lists our observed XRD data. Figure 5 shows the powder XRD traces of 2:1 Mg:Al LDH cobalticyanide and 2:1 Mg:Al nitroprusside. The observed basal spacings of 10.75 Å for the 2:1 Mg:Al LDH cobalticyanide and 11.09 Å for the 2:1 Mg:Al LDH nitroprusside are consistent with the values previously reported.\(^{19,29}\) The XRD trace for the 2:1 Mg:Al LDH nitroprusside
seems unusual in that the observed 006 reflection is of greater intensity than the 003 reflection. We have, however, observed similar intensity ratios in other similar systems, e.g., LDH ferrocyanide.

Table 4 lists the results of the elemental analysis of these samples. Since this table combines data obtained by completely different techniques (ICP, microanalytical GC) in different laboratories, the agreement between observed and predicted M:C and M:N ratios is satisfactory. Perhaps the most interesting result is the absence of any extensive loss of N (and hence NO from the nitroprusside. The Al:Fe ratio in the LDH nitroprusside is found to be 3.57. This value falls between the values expected for complete intercalation of nitroprusside (2.00) and ferrocyanide (4.00). The LDH cobalticyanide exhibits a Al:Co ratio of 3.44, close to the theoretical value of 3.00, indicating nearly complete replacement of chloride by cobalticyanide. In each case, the Mg:Al ratio falls below the expected value of 2.00, implying an enrichment in Al relative to Mg during intercalation. Such results have been reported by other workers for LDHs intercalated with similar anions.\textsuperscript{21, 26, 28}

We performed TGA/DTA analysis on the Mg:Al LDH cobalticyanide, nitroprusside and ferricyanide for comparison. All three of the samples showed the expected weight loss between 100 and 200 °C normally associated with loss of interlayer water. The rest of the thermograms are more complicated and are under further investigation.\textsuperscript{31}
Table 3. Observed Powder XRD Spacings for Nitrate- and Nickelocyanide-Containing Mg:Al LDHs. Literature values listed in parentheses. (hkl assignment based on ref. 36).

<table>
<thead>
<tr>
<th>Anion</th>
<th>$d_{003}$</th>
<th>$d_{006}$</th>
<th>$d_{012}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>7.87 (7.86)</td>
<td>3.96</td>
<td>2.65</td>
</tr>
<tr>
<td>$\left[\text{Co(CN)}_6\right]^{3-}$</td>
<td>10.75 (10.8)</td>
<td>5.44</td>
<td>2.61</td>
</tr>
<tr>
<td>$\left[\text{Fe(CN)}_5(\text{NO})\right]^{2-}$</td>
<td>11.09 (11.0)</td>
<td>5.57 (5.47)</td>
<td>2.59 (2.65)</td>
</tr>
</tbody>
</table>

Figure 5. Powder XRD patterns for (a) 2:1 Mg:Al LDH chloride, (b) 2:1 Mg:Al LDH cobalticyanide, and (c) product from attempted preparation of 2:1 Mg:Al LDH nitroprusside. (Asterisks (*) denote standard; cross (+) denotes contaminant Mg:Al LDH carbonate phase.)
Table 4. Elemental Analysis Results of Mg:Al LDH Compounds.

<table>
<thead>
<tr>
<th></th>
<th>%Mg</th>
<th>%Al</th>
<th>%M</th>
<th>%C</th>
<th>%N</th>
<th>%H</th>
<th>Mg:Al</th>
<th>Al:M</th>
<th>C:M</th>
<th>N:M</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Co(CN)₅)⁻</td>
<td>15.25</td>
<td>10.13</td>
<td>6.22</td>
<td>6.86</td>
<td>7.37</td>
<td>1.67</td>
<td>3.44</td>
<td>5.55</td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td>(Fe(CN)₅(NO)⁻)²</td>
<td>14.56</td>
<td>9.36</td>
<td>5.50</td>
<td>7.57</td>
<td>9.04</td>
<td>3.22</td>
<td>1.72</td>
<td>3.57</td>
<td>6.25</td>
<td>6.67</td>
</tr>
</tbody>
</table>

Deformation of Intercalated Cobalticyanide

For cobalticyanide, ferrocyanide, and the 2142 and 1936 cm⁻¹ bands of nitroprusside, the LDH intercalate frequencies are very close to those in aqueous solution, implying similar hydrogen bonding to the terminal N lone pair. We have previously shown that the splitting of the ν(CN) peak of intercalated ferrocyanide is attributable to the T₁u mode in O₅h symmetry splitting into separate A₂u and Eₘ components in D₃d symmetry, indicating distortion of the anion force-field in the LDH interlayer. Both of these components are present in the conventional spectrum, but in the oriented spectrum the A₂u component, being polarized in the direction of polarization of the beam, is suppressed. Close inspection of the non-oriented ν(CN) peak of Mg:Al LDH cobalticyanide (Figure 3) reveals very minor, yet noticeable and reproducible splitting. The corresponding peak in the oriented IR spectrum shows suppression of the higher frequency component, resulting in a symmetric peak. This small splitting seen in the non-oriented spectrum and the suppression of the c-polarized component upon orientation indicates slight distortion, much less than that seen for intercalated ferrocyanide, from local O₅h symmetry of the cobalticyanide. Some such distortion is of necessity imposed by H-bonding to layer OH, and may or may not be accompanied by geometrical distortion. We suggest this difference in behavior is due to the three-minus cobalticyanide forming weaker hydrogen bonds with the layer than the four-minus ferrocyanide.\footnote{22}

Kikkawa was the first to suggest that the ferrocyanide anion intercalated into Mg:Al LDH with its three-fold symmetry axis perpendicular to the cation sheets.\footnote{27} Utilizing Miyata’s reported sheet thickness of 4.8Å,\footnote{35} Kikkawa calculated the gallery height of Mg:Al LDH ferrocyanide to be approximately 6 Å. Similar treatment of the Mg:Al LDH cobalticyanide was reported by Suzuki and Ono.\footnote{37} We have refined this method by utilizing the scheme shown in Figure 6. We have defined an axis terminated by hydrogen atoms in the cation sheets and containing one of the anions’ NCNC axes.
Based on the crystal structure of potassium cobalticyanide reported by Curry and Runciman, the average Co-C distance is 1.89Å and the average C-N distance is 1.17Å, yielding a cobalticyanide 4-fold axis length of 6.12Å. Based on the crystal structure of potassium ferrocyanide reported by Taylor et al. we assume N—H hydrogen bond lengths of 2.84 Å. We use an idealized H-N-C bond angle of 180°, because of sp hybridization at N. These values yield an overall hydrogen atom to hydrogen atom axis distance of approximately 11.08Å and a corresponding gallery height between the hydrogen atom lanes of 11.08Å/√3 or 6.84 Å. The vertical distance between H atoms on either side of the sheet, from Allmann's results of single crystal samples of hydrotalcite, is calculated to be 4.77Å. Thus, the sum of our newly defined gallery height, comprising the space between the atomic centers of opposing hydrogen layers and the layer thickness, is 11.15Å; this is reasonably close to the observed powder XRD value of 10.75Å. The difference between the calculated and observed d_{001} spacing could well be caused by the presence of shorter or slightly skewed bonds between the layer and anion.
This work shows that spectroscopic methods may be used to help elucidate the nature of interaction between the intercalated anion and cation sheets in certain LDH systems. Using oriented IR, we have demonstrated that, like ferrocyanide, cobalticyanide experiences some deformation from $O_h$ symmetry upon insertion into LDH. The extent of this deformation is much less for cobalticyanide than for ferrocyanide, presumably due to the lower anion charge on cobalticyanide.

From “Spectroscopic Polarization of Hexacyanoruthenate(II) anions Intercalated in Mg:Al Layered Double Hydroxides” to be submitted to Chemistry of Materials. Collaborative effort with Paul S. Braterman and Joseph W. Boclair. Layered materials containing the $[\text{Ru(CN)}_6]^{4-}$ anion were synthesized and characterized by conventional and oriented IR by the author. Powder XRD data for the LDH hexacyanoruthenate(II) compounds (both the 2:1 and the 3:1) were obtained by Joseph W. Boclair. Relevant data for the LDH ferrocyanide compounds were referenced from previously published works.

Abstract

Hexacyanoruthenate(II) anions were intercalated into Mg:Al layered double hydroxides (LDH) having Mg:Al ratios of 2:1 and 3:1. The $[\text{Ru(CN)}_6]^{4-}$ anion is shown to intercalate into layered double hydroxides in the same manner as other hexacyano anions, such as ferrocyanide and cobalticyanide, with its three-fold rotational axis perpendicular to the hydroxide sheets. The FTIR spectra of ruthenocyanide LDHs are compared with those of ferrocyanide LDHs and differences in the polarization in the $\nu$(CN) of the intercalated anion in relation to the Mg:Al ratio are discussed.
Introduction

In this Communication, we describe the incorporation of hexacyanoruthenate(II) (ruthenocyanide) into the interlayer of Mg:Al LDH as well as differences in the polarization of the v(CN) bands in the FTIR spectrum of both ferrocyanide and ruthenocyanide dependent on the charge density of the hydroxide layers. Exchange reactions between the parent LDH chloride and either K₄Fe(CN)₆ or K₄Ru(CN)₆ were performed as described previously.²⁰

Results and Discussion

The powder XRD patterns for 2:1 and 3:1 Mg:Al LDH ferrocyanide are very similar and discussed elsewhere.²³ ³⁰ Our own XRD patterns for these materials are consistent with those previously reported (Table 5). Table 5 also lists the observed XRD peaks for 2:1 and 3:1 Mg:Al LDH ruthenocyanide. The 2:1 LDH ruthenocyanide exhibits a basal spacing of 10.62 Å while the 3:1 materials exhibits a basal spacing of 10.52 Å. These basal spacings are consistent with the ruthenocyanide anion intercalating into LDH with its three-fold symmetry axis perpendicular to the hydroxide layers; behavior that is well documented for octahedral anions in LDH.²⁰, ²³, ²⁷

<table>
<thead>
<tr>
<th>Mg:Al ratio</th>
<th>Anion</th>
<th>d₁₀₀₃</th>
<th>d₀₀₆</th>
<th>d₂₀₀₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>[Fe(CN)₆]₄⁺</td>
<td>10.77</td>
<td>5.34</td>
<td>2.75</td>
</tr>
<tr>
<td>3:1</td>
<td>[Fe(CN)₆]₄⁺</td>
<td>10.90</td>
<td>5.50</td>
<td>2.62</td>
</tr>
<tr>
<td>2:1</td>
<td>[Ru(CN)₆]₄⁺</td>
<td>10.62</td>
<td>5.37</td>
<td>----</td>
</tr>
<tr>
<td>3:1</td>
<td>[Ru(CN)₆]₄⁺</td>
<td>10.52</td>
<td>5.37</td>
<td>----</td>
</tr>
</tbody>
</table>

We have shown previously that, by depositing a thin film of LDH onto a barium fluoride disk, it is possible to obtain oriented infrared spectra for 2:1 Mg:Al LDH containing ferrocyanide,³⁰ cobalticyanide and nitroprusside. We applied this technique to 3:1 Mg:Al LDH ferrocyanide. The conventional FTIR spectrum of 3:1 Mg:Al LDH ferrocyanide shows a distinct splitting of the T₁₉g v(CN) of ferrocyanide initially very similar to that of the 2:1 material. The peak has a maximum value at 2042 cm⁻¹ with an unresolved high
frequency shoulder at approximately 2058 cm\(^{-1}\) (compared with the values 2034 cm\(^{-1}\) and 2046 cm\(^{-1}\) respectively for the 2:1 LDH ferrocyanide). Upon orientation, the high frequency component is suppressed, leaving a more or less symmetric peak centered at 2043 cm\(^{-1}\). This is in contrast to 2:1 Mg:Al LDH ferrocyanide where the lower frequency component is c-polarized and suppressed on orientation.

Comparison of both the oriented and conventional FTIR spectra of 2:1 and 3:1 Mg:Al LDH ruthenocyanide shows a remarkable similarity to LDH ferrocyanide. The 2:1 LDH ruthenocyanide shows a split \(\nu(CN)\) with a maximum at 2154 cm\(^{-1}\) and an unresolved low-frequency shoulder near 2145 cm\(^{-1}\). The 2154 cm\(^{-1}\) maximum is nearly identical to the observed value in aqueous solution (2155 cm\(^{-1}\)), as expected. Upon orientation, the higher frequency component of the \(\nu(CN)\) is suppressed leaving a symmetric peak centered at 2145 cm\(^{-1}\); completely analogous to the ferrocyanide case. The 3:1 Mg:Al LDH ruthenocyanide also mirrors the behavior of the ferrocyanide with a reversal of the \(a,b\)- and \(c\)-polarized components of \(\nu(CN)\) versus the 2:1 material.

Conclusions

We have shown in this work that hexacyanoruthenate(II) (ruthenocyanide) intercalates into Mg:Al LDH having Mg:Al ratios of 2:1 and 3:1. We have demonstrated that the ruthenocyanide anion behaves in a manner completely analogous to the ferrocyanide anion under the same conditions. Our method for observing \(a,b\)-polarized FTIR spectra has been applied to these materials and differences in the polarization of the \(\nu(CN)\) of both ferrocyanide and ruthenocyanide are reported in changing the charge density of the cation-hydroxide layer. The exact origin of this change is polarization is uncertain, but we speculate that it may be caused by the distinct differences in local environment caused by the change in charge density. Such differences may well be exploitable in the realm of catalyst preparation.
From “Tetracyano-Nickelate(II), -Palladate(II), and -Platinate(II) Anions Intercalated Into Mg:Al Layered Double Hydroxides: Effect of Layer Charge Density on Orientation” to be submitted to Journal of The American Chemical Society. Collaborative effort with Paul S. Braterman and Joseph W. Bocclair. Synthesis of all compounds and characterization via conventional and oriented IR was performed by the author; characterization by powder XRD, extra experiments with potassium tetracyanonickelate and aluminum chloride, plus some extra IR studies performed by Joseph W. Bocclair.

Abstract

The square-planar tetracyano-nickelate(II), -palladate(II), and platinate(II) anions were intercalated into both 2:1 and 3:1 Mg:Al layered double hydroxides (LDH). The basal spacings in the 2:1 hosts are approximately 11 Å, indicating that the anions are inclined approximately 75 degrees relative to the hydroxide layers, while in the 3:1 hosts the square-planar anions have enough space to lie more nearly parallel to the LDH cation layers, giving basal spacings of approximately 8 Å. We believe this to be the first report of incorporation of acyclic square planar complexes, and of Pd and Pt complexes of any kind, into LDH.

Introduction

In this Communication we describe the uptake of [Ni(CN)₄]²⁻, [Pd(CN)₄]²⁻, and [Pt(CN)₄]²⁻ into LDH, the first examples of incorporation of simple (non-macrocyclic) square planar complexes into LDH, report the first case of incorporation (as opposed to surface uptake) of a Pt complex of any kind, and demonstrate that charge density of the LDH greatly impacts the orientation of intercalated square-planar anions.
Results and Discussion

The powder X-ray diffraction patterns for 2:1 Mg:Al LDH \([\text{Ni(CN)}_4]^2\) shows \(d_{003}\) and \(d_{006}\) reflections at 11.05 and 5.60 Å respectively.[4] This material also shows another spacing of much lower intensity at 7.72 Å which we assign to contamination by the well-known LDH carbonate phase. The observed basal spacing of 11.05 Å in the 2:1 LDH nickelocyanide indicates that the anion is inclined at an appreciable angle relative to the cation sheets. Based upon crystal XRD data for K\(_2\)Ni(CN)\(_4\)[41] and the van der Waals radius of nitrogen,[42] the square-planar tetracyanonickelate(II) anion can be regarded as a rounded square approximately 6.38 Å per side and approximately 3 Å thick. This model for the [Ni(CN)\(_4\)]\(^2\) anion coupled with the accepted thickness of a Mg:Al LDH sheet of approximately 4.8 Å\(^3\)\(^5\) yields the square-planar anions oriented at an angle of approximately 75° relative to the cation sheets. Simple geometric arguments imply that this tilting is imposed on the nickelocyanide by the high charge density of the metal hydroxide sheet. Similar effects have been demonstrated by Kuk and Huh for the intercalation of anthraquinone sulfonate ions into Zn:Al LDHs\(^43\) and by Labajos, Rives and Ulibarri for carbonate-containing Ni(II):Al LDHs.\(^44\)

The full-scale conventional and oriented FTIR spectra of 2:1 Mg:Al LDH nickelocyanide support the notion of an inclined square-planar anion. The conventional FTIR spectrum clearly shows a splitting of the \(v(\text{CN})\) peak with a maximum at 2122 cm\(^{-1}\) and an unresolved lower frequency component of comparable intensity at around 2110 cm\(^{-1}\), indicating deviation from ideal D\(_{4h}\) symmetry. An inclined anion would occupy a site whose symmetry is at most C\(_{2v}\), without necessarily distorting the geometry of the anion itself. The oriented FTIR spectrum, which suppresses c-axis polarized absorption, shows a single symmetric band centered at 2124 cm\(^{-1}\). These data are in agreement with the value for aqueous solutions of the tetracyanonickelate(II) anion (2123.5 cm\(^{-1}\)),\(^45\) and reminiscent of the orientational effects observed with ferrocyanide.\(^30\) The full-scale FTIR spectrum of 2:1 Mg:Al LDH nickelocyanide shows a sharp, high frequency \(v(\text{OH})\) at 3642 cm\(^{-1}\), clearly distinct from the sharp \(v(\text{OH})\) of Mg(OH)\(_2\),\(^46\) which we find at 3700 cm\(^{-1}\). We therefore explain this high frequency band as non-hydrogen bonded OH in the LDH. Both the \(v(\text{OH})\) and \(v(\text{CN})\) region of both the conventional and oriented FTIR spectra of 2:1 Mg:Al LDH nickelocyanide are presented in Figure 7.
Figure 7. FTIR spectra a) conventional, b) oriented, of 2:1 Mg:Al LDH [Ni(CN)₄]²⁻.
Note scale change.

The powder XRD diffractogram for 3:1 Mg:Al LDH nickelocyanide shows \( d_{003} \) and \( d_{006} \) spacings at 8.00 and 3.98 Å respectively. Subtracting the cation layer thickness of 4.8 Å yields an interlayer distance of 3.3 Å, much less than the interlayer distance of 6.2 Å in the 2:1 material, and close to the expected thickness of the nickelocyanide anion itself. Thus the XRD data suggest that, in the 3:1 LDH, the \([\text{Ni(CN)}_4]^2\) orients itself parallel, or very nearly so, to the cation layers. This difference in orientation between the 2:1 and 3:1 materials can clearly be attributed to the difference in layer charge density between the two.

The conventional FTIR spectrum of 3:1 Mg:Al LDH nickelocyanide shows two peaks in the \( \nu(\text{CN}) \) region, one at 2124 cm\(^{-1}\), corresponding to the normally active mode of nickelocyanide and observed in the 2:1 LDH and, in this case, a new peak near 2170 cm\(^{-1}\). The 2124 cm\(^{-1}\) peak shows less splitting in the conventional IR of the 3:1 LDH than its counterpart in the 2:1 LDH. The new peak near 2170 cm\(^{-1}\) appears somewhat sporadically in the FTIR spectra of 3:1 LDH nickelocyanides. This 2170 cm\(^{-1}\) peak is of varying intensity and sometimes not present at all. Very similar behavior is shown, in LDH ferrocyanide systems, by bands we attribute to cubic ferrocyanide species formed by reaction of ferrocyanide with cations from the hydroxide sheets.\(^{47}\) We have found in preliminary experiments that treatment of potassium nickelocyanide with magnesium
chloride in water gives no insoluble product but treatment with aluminum chloride yields a small amount of an insoluble, pale blue product, with a complex FTIR spectrum, including $\nu$(CN) at 2170 cm$^{-1}$. At this time, we have no explanation why a material formally deficient in Al$^{3+}$ would surrender some of its aluminum to form this other species.

We have intercalated tetracyanoplatinate(II) into both 2:1 and 3:1 Mg:Al LDH. The results for this anion intercalated into Mg:Al LDH parallel those seen for the nickelocyanide and are summarized in Tables 6 and 7. The powder XRD data for [Pt(CN)$_4$]$^{2-}$-containing LDHs show $d_{003}$ spacings of 10.92 and 8.00 Å respectively in 2:1 and 3:1 Mg:Al LDHs. The 2:1 Mg:Al LDH [Pt(CN)$_4$]$^{2-}$ XRD trace shows an unusually intense narrow peak at 5.84 Å, near, possibly on top of, the expected $d_{006}$ spacing. This intense peak is presumably related to the intense scattering power of platinum. The conventional infrared spectrum of the 2:1 Mg:Al LDH [Pt(CN)$_4$]$^{2-}$ shows $\nu$(CN) at 2133 cm$^{-1}$. [5]


<table>
<thead>
<tr>
<th>Mg:Al</th>
<th>M$^{n+}$</th>
<th>$d_{003}$</th>
<th>$d_{006}$</th>
<th>$d_{201}$</th>
<th>$d_{110}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>Ni</td>
<td>11.05 (7.72)$^a$</td>
<td>5.59</td>
<td>2.59</td>
<td>1.52</td>
</tr>
<tr>
<td>3:1</td>
<td>Ni</td>
<td>8.00</td>
<td>3.98</td>
<td>2.62</td>
<td>1.53</td>
</tr>
<tr>
<td>2:1</td>
<td>Pd</td>
<td>11.09 (7.91)$^a$</td>
<td>5.56</td>
<td>2.61</td>
<td>1.53</td>
</tr>
<tr>
<td>3:1</td>
<td>Pd</td>
<td>8.09</td>
<td>4.02</td>
<td>2.62</td>
<td>1.54</td>
</tr>
<tr>
<td>2:1</td>
<td>Pt</td>
<td>10.65</td>
<td>5.85</td>
<td>2.62</td>
<td>1.52</td>
</tr>
<tr>
<td>3:1</td>
<td>Pt</td>
<td>8.15</td>
<td>4.06</td>
<td>2.63</td>
<td>2.1</td>
</tr>
</tbody>
</table>

$^a$ denotes probable LDH carbonate $d_{003}$. 
Table 7. Conventional FTIR data for Mg:Al LDH $[\text{M}^{\text{II}(CN)_4}]^{2-}$. Values given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Mg:Al</th>
<th>M$^{\text{II}}$</th>
<th>$\nu$(OH)</th>
<th>$\delta$(OH)</th>
<th>$\nu$(CN)</th>
<th>lattice peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>Ni</td>
<td>3488,3648</td>
<td>1630</td>
<td>2123</td>
<td>669,555, 448</td>
</tr>
<tr>
<td>3:1</td>
<td>Ni</td>
<td>3496</td>
<td>1639</td>
<td>2123</td>
<td>630,414</td>
</tr>
<tr>
<td>2:1</td>
<td>Pt</td>
<td>3469,3642</td>
<td>1628</td>
<td>2134</td>
<td>667,553,448</td>
</tr>
<tr>
<td>3:1</td>
<td>Pt</td>
<td>3469</td>
<td>1642</td>
<td>2134</td>
<td>638,412</td>
</tr>
<tr>
<td>2:1</td>
<td>Pd</td>
<td>3436,3634</td>
<td>1619</td>
<td>2136</td>
<td>688, 554, 448</td>
</tr>
<tr>
<td>3:1</td>
<td>Pd</td>
<td>3500</td>
<td>1621</td>
<td>2135</td>
<td>686, 616, 414</td>
</tr>
</tbody>
</table>

We have also prepared 2:1 and 3:1 Mg:Al LDH tetracyanopalladate(II) by the same method, and characterized these materials by their XRD patterns (see Table 6) and FTIR spectra (see Table 7), which are fully consistent with those seen for the tetracyanonickelete(II) and -platinate(II) LDH. The 3:1 Mg:Al LDH $[\text{Pd(CN)}_4]^{2-}$ shows a basal spacing of 8.09 Å while the 2:1 shows a basal spacing of 11.09 Å, with another peak at 7.91 Å, similar in intensity to the 7.72 Å peak seen in nickelocyanide case. The intercalated $[\text{Pd(CN)}_4]^{2-}$ anion exhibits $\nu$(CN) at 2135 cm$^{-1}$ in the 3:1 LDH and at 2136 cm$^{-1}$ in the 2:1 LDH, identical to the value reported for the aqueous species (2136 cm$^{-1}$).26 The 2:1 (but not 3:1) LDH $[\text{Pd(CN)}_4]^{2-}$ also shows the high frequency $\nu$(OH) at 3634 cm$^{-1}$ seen in both the 2:1 (but not the 3:1) LDH $[\text{Ni(CN)}_4]^{2-}$ and $[\text{Pt(CN)}_4]^{2-}$.

Conclusions

We have shown in this work an unambiguous case of intercalation of square-planar anions into Mg:Al LDH. A claim to have incorporated square planar $[\text{NiCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ is problematic,5 and in disagreement with the well known chemistry of Ni(II) and Co(II) in relation to chloride.49 Our results clearly demonstrate the dramatic effect of the layer charge density on the orientation of those anions upon intercalation. This work has clear implications for the use of LDHs as catalyst supports and precursors as well as demonstrating the subtlety of relationships between the layers and exchangeable anions of LDH systems, and providing the first examples of uptake of palladium and platinum complexes into the interlayer space of LDH.
From “Physical and Chemical Interactions Between Mg:Al Layered Double Hydroxides and Hexacyanoferrate” submitted for publication to Journal of Solid State Chemistry. Collaborative effort with Joseph W. Boclair, Paul S. Braterman, Zhiming Wang, and Faith Yarberry. Data for LDH hexacyanocobaltate(III), along with preliminary synthesis and IR characterization of potassium-magnesium-ferrocyanide compounds performed by the author; all other experiments performed by the co-authors of the paper.

Abstract

The physical and chemical interactions of ferrocyanide (potassium and ammonium salts) and ferricyanide (potassium salt) with Mg:Al layered double hydroxides (LDH) (having Mg:Al ratios of 2 and 3) are investigated using powder XRD and FTIR spectroscopy. Physically, the potassium ferricyanide is shown to intercalate with a small local field deformation similar to that seen for hexacyanocobaltate(III) in similar materials. Chemically, the reduction of ferricyanide to ferrocyanide upon intercalation is confirmed. Physical interactions of ferrocyanide with 3:1 LDH are shown spectroscopically to include the possible generation of anions in differing environments. Chemically, ferrocyanide is shown to generate cubic ferrocyanides (of the type $M\cdot MgFe(CN)_6$, where $M = K^+$ or $NH_4^+$) under conditions where free $Mg^{2+}$ is likely present in solution, namely solutions with a pH lower than ~7.5. It is shown that the reported 2112 cm$^{-1}$ band of chemically altered LDH ferrocyanide is indeed due to interlayer ferricyanide, but that the 2080 cm$^{-1}$ band is due to the cubic material.

Introduction

The applications and importance of LDH have recently been reviewed both in general, and with particular application to the incorporation of anionic metal complexes.

Cyanide, in various forms, is thought to have played major roles in the origins of life. Generally, cyanides seem to provide the only realistic synthetic routes to purines and pyrimidines under early Earth conditions. For instance, Oró and coworkers have demonstrated the formation of adenine from ammonium cyanide solutions.
double hydroxides have also been invoked in studies of the origins of life.\textsuperscript{19, 54, 55} Our interest in this area arises from the possible concentration and/or activation of cyanide from solution by LDH.\textsuperscript{56} Cyanide has been shown to be easily introduced into LDH systems through intercalation of metallacyano-complexes such as ferricyanide,\textsuperscript{19, 24-26, 57} ferrocyanide,\textsuperscript{19, 21-27, 30} nitroprusside,\textsuperscript{19, 20} and cobalticyanide.\textsuperscript{20, 29} Thus, the behavior of complex cyanides in the presence of LDH is a matter of some importance in a number of areas.

In the cases of ferricyanide and ferrocyanide, intercalation of the anion into the LDH may be accompanied by changes in either the oxidation state of the anion and/or the structure of the LDH system itself. The situation regarding ferrocyanide intercalation is the more interesting situation of the two. Rives\textsuperscript{22} ascribes a band near 2080 cm\textsuperscript{-1}, in both the Mg:Al and Zn:Al systems, to intercalated ferricyanide formed by oxidation of ferrocyanide, for which Hansen \textit{et al.}\textsuperscript{23} report a frequency of 2112 cm\textsuperscript{-1}. Hansen and coworkers\textsuperscript{23} also reported, under certain experimental conditions, the presence of a $v$(CN) absorption near 2080 cm\textsuperscript{-1} and suggested (correctly as we shall see) that this 2080 cm\textsuperscript{-1} species could be some form of cubic ferrocyanide.

We show in this work that, upon intercalation into either 2:1 or 3:1 Mg:Al LDH, ferricyanide undergoes a variable amount of reduction to ferrocyanide, with cyanide itself presumably acting as the reducing agent. We extend our previous use of oriented FTIR spectroscopy to 2:1 and 3:1 Mg:Al LDH ferricyanide and 3:1 Mg:Al LDH ferrocyanide. Intercalated ferricyanide is shown to exhibit a small deviation from local $O_h$ symmetry similar to that found\textsuperscript{20} in intercalated cobalticyanide. The oriented spectrum of 3:1 Mg:Al LDH ferrocyanide shows a switch in the relative frequencies of the $a,b$- and $c$-polarized components relative to the 2:1 case.

We find that when LDH is exposed to or prepared in the presence of solutions of potassium ferrocyanide, under conditions where free Mg$^{2+}$ may exist in solution, two types of material may be formed in varying ratios. The initial product contains intercalated ferrocyanide, while in the presence of free Mg$^{2+}$, cubic material of nominal composition $K_2MgFe(CN)_6$ is also produced. We also find that treatment of Mg:Al LDH with solutions of ammonium ferrocyanide generates intercalated ferrocyanide and ammonium magnesium ferrocyanide [$(NH_4)_2MgFe(CN)_6$] in all cases. The ability of
these LDH systems to spontaneously generate materials containing cyanides in varied
environments with, perhaps, different reactivities places them in good stead to promote
and/or control certain cyanide reactions of possible prebiotic importance. The material
with [v(CN) = 2080 cm⁻¹] formed from exposure of LDH to ferrocyanide, under
conditions where free Mg²⁺ is expected to be present and previously assigned²² as LDH
ferricyanide, would appear to be identical with our cubic material while that formed
during a vigorous dehydration process [v(CN) = 2112 cm⁻¹]²³ is comparable to
conventionally prepared LDH ferricyanide.

**Experimental**

The starting materials, 2:1 and 3:1 Mg:Al LDH chloride, [Mg₂Al(OH)₆Cl] and
Mg₃Al(OH)₈Cl, were prepared according to the previously described procedure.⁵⁶ ²⁰
Ferrocyanide- and ferricyanide-exchanged materials were generally prepared as pale
cream and yellow colored solids, respectively. In cases where we desired to investigate
the formation of cubic materials, the LDH chlorides were exposed to excess 0.2M
ferrocyanide solutions, under a slow stream of nitrogen. In all cases, exchanges were
performed using starting material which had been kept damp in a sealed centrifuge tube
and reaction times varied between 18 and 24 hours. During the reaction and drying
periods, and subsequent storage, all ferro- and ferricyanide containing reaction mixtures
and products were protected from light by aluminum foil in order to prevent unwanted
photolytic reactions involving the anions.

Following exchange with the appropriate anion, the products were repeatedly
washed and collected via centrifuge and allowed to dry in an evacuated desiccator over
molecular sieves at ambient temperature. Infrared and powder XRD data were collected
as described elsewhere.⁵⁸ ⁶⁰

Potassium magnesium ferrocyanide (K₂MgFe(CN)₆) was prepared by slowly
adding, via an addition funnel, 100 mL of a 0.1 MgCl₂ solution to 100 mL of a 0.1M
K₄Fe(CN)₆ solution over a period of approximately 45 minutes. The reaction mixture
was kept under a slow stream of nitrogen and stirred magnetically for the duration of the
addition. The reaction vessel was covered in aluminum foil to prevent photolysis of the
ferrocyanide solution and/or the product. The resulting white solid was then collected
and repeatedly washed via centrifuge. Ammonium magnesium ferrocyanide 

diagram

\[ (\text{NH}_4)_2\text{MgFe(CN)}_6 \] was prepared similarly.

**Results and Discussion**

*Physical Interaction with Ferricyanide*

Figure 8 shows the observed powder XRD patterns for 2:1 and 3:1 Mg:Al LDH ferricyanide. The observed basal spacings are 11.18 Å for the 2:1 and 10.99 Å for the 3:1. These spacings indicate that the ferricyanide anion intercalates with its three-fold axis perpendicular to the hydroxide layers. Kikkawa first proposed this mode of intercalation for ferrocyanide in LDH and it appears from the basal spacings to be the preferred anion orientation in every M(CN)_6^- intercalated LDH reported to date.  

The main peaks from each of these diffraction patterns are compiled in Table 8.

<table>
<thead>
<tr>
<th>Mg:Al</th>
<th>(d_{003})</th>
<th>(d_{006})</th>
<th>(d_{009})</th>
<th>(d_{012})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>11.18</td>
<td>5.57</td>
<td>3.71</td>
<td>2.63</td>
</tr>
<tr>
<td>3:1</td>
<td>10.99</td>
<td>5.52</td>
<td>3.66</td>
<td>2.57</td>
</tr>
</tbody>
</table>

\((7.89)\)
Figure 8. Powder XRD patterns of (a) 2:1 and (b) 3:1 Mg:Al LDH ferricyanide.

Table 9. FTIR data for 2:1 and 3:1 Mg:Al LDH ferricyanide. All values in cm\(^{-1}\). The presence of \(\nu(C=O)\) is due to adventitious carbonate.

<table>
<thead>
<tr>
<th>Mg:Al</th>
<th>(\nu(OH))</th>
<th>(\delta(OH))</th>
<th>(\nu(CN))</th>
<th>(\delta(MCN))</th>
<th>(\nu(C=O))</th>
<th>lattice peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>3544, 3436</td>
<td>1622</td>
<td>2117, 2035</td>
<td>553</td>
<td>1359</td>
<td>674, 448</td>
</tr>
<tr>
<td>3:1</td>
<td>3495</td>
<td>1632</td>
<td>2118, 2037</td>
<td>-----</td>
<td>1371</td>
<td>614, 414</td>
</tr>
</tbody>
</table>

Figures 9 and 10 present both the conventional and oriented FTIR spectra of 2:1 and 3:1 Mg:Al LDH ferricyanide. In each case, two \(\nu(CN)\) peaks are observed; one near 2112 cm\(^{-1}\) and the other near 2045 cm\(^{-1}\). Hexacyano-anions, intercalated into LDH, have been
shown\textsuperscript{23,29} to exhibit infrared spectra virtually identical in position to the aqueous anion. Our own data and literature reports\textsuperscript{61} indicate that aqueous ferricyanide exhibits a single $\nu$(CN) IR band at or near 2111 cm$^{-1}$. We therefore assign the 2112 cm$^{-1}$ species as intercalated ferricyanide. We attribute the 2045 cm$^{-1}$ peak to ferrocyanide obtained by reduction of the ferricyanide and discuss it further in the following section. The intercalated ferricyanide shows a slight splitting of the $\nu$(CN), similar in magnitude to that seen\textsuperscript{20} for cobalticyanide. Such similarities in the spectroscopic properties of cobalticyanide and ferricyanide are hardly surprising, given the similar sizes and charges of the two anions, one would expect their interaction with the LDH cation layers to be similar. Orientation\textsuperscript{30} of 2:1 LDH ferricyanide yields a broad, symmetric peak centered at 2111 cm$^{-1}$. Similar results are seen for the 3:1 LDH ferricyanide. Significant peaks of the FTIR spectra for 2:1 and 3:1 Mg:Al LDH ferricyanide are summarized in Table 9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Full-scale FTIR spectra of (a) 2:1 and (b) 3:1 Mg:Al LDH ferricyanide.}
\end{figure}
Figure 10. Expanded-scale FTIR spectra, conventional (upper) and oriented (lower), of (a) 2:1 and (b) 3:1 LDH ferricyanide.

Physical Interaction With Ferrocyanide

The physical interaction of ferrocyanide with 2:1 Mg:Al LDH has been previously discussed in detail and is well understood. In this case, the $T_{1u}$ mode of octahedral ferrocyanide is split into $E_u$ and $A_{2u}$ modes in $D_{3h}$ upon intercalation into LDH. Thus, the FTIR spectrum of the 2:1 Mg:Al LDH ferrocyanide shows two $\nu$(CN) modes; one at 2035 cm$^{-1}$ and the other at 2045 cm$^{-1}$. The oriented FTIR spectrum shows that the $A_{1u}$ ($z$-polarized) absorption is that observed at the lower frequency.

Figure 11 shows the observed powder XRD patterns for 3:1 Mg:Al LDH chloride and ferrocyanide. The ferrocyanide-exchanged material shows a basal spacing of 10.99 Å, compared with 10.77 Å for the 2:1 LDH ferrocyanide. (The small difference in basal spacings between the 2:1 and 3:1 Mg:Al LDH ferrocyanides is possibly related to
Figure 11. Powder XRD patterns of 3:1 Mg:Al LDH (a) chloride and (b) ferrocyanide. Variations in hydration state.) Such a spacing is consistent with the intercalated anion being in the expected orientation of having a three-fold axis perpendicular to the hydroxide layers.

Table 10 compiles the significant XRD peaks of the 3:1 Mg:Al LDH ferrocyanide. The conventional and oriented FTIR spectra of 2:1 Mg:Al LDH ferrocyanide are presented in Figure 12 for the sake of comparison together with those of
the corresponding 3:1 system, reported here for the first time. Dramatic differences are observed. Comparison of the oriented spectra of the 2:1 and 3:1 LDH ferrocyanides also shows that the relative polarization of the 2035 and 2045 cm\(^{-1}\) species is reversed in the 3:1 case relative to the 2:1, with the 2045 cm\(^{-1}\) peak being suppressed on orientation in the 3:1 material. Thus the lower frequency band in each species correlates with the higher frequency band in the other. The reasons for this effect are not clear. In the conventional FTIR spectrum, the 3:1 Mg:Al LDH ferrocyanide shows a more complex \(\nu(CN)\) region than the 2:1 LDH. In addition to the peaks at 2035 and 2045 cm\(^{-1}\), there are also a number of less intense and less well-defined peaks throughout this region. Such a complex \(\nu(CN)\) spectrum suggests a situation where ferrocyanide is in several distinct interlayer environments. Interlayer ferrocyanide ions in 3:1 LDH are expected to be positioned further away from each other than in the 2:1 case. The extra room in the 3:1 case may well provide a more diverse range of opportunities for the anion to hydrogen bond to non-equivalent lattice OH groups. Significant peaks of the FTIR spectra for 2:1 and 3:1 Mg:Al LDH ferrocyanide are summarized in Table 11.

Table 10. Powder XRD data (\(d\)-spacings given in Å) for 3:1 Mg:Al LDH ferricyanide and chloride.

<table>
<thead>
<tr>
<th>Anion</th>
<th>(d_{002})</th>
<th>(d_{006})</th>
<th>(d_{009})</th>
<th>(d_{112})</th>
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</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>7.80</td>
<td>3.98</td>
<td>1.92</td>
<td>1.54</td>
</tr>
<tr>
<td>[Fe(CN(_6))(^4)](^+)</td>
<td>10.90</td>
<td>5.50</td>
<td>3.68</td>
<td>2.58</td>
</tr>
</tbody>
</table>

Table 11. FTIR data for 2:1 and 3:1 Mg:Al LDH ferrocyanide. All values in cm\(^{-1}\). The presence of \(\nu(C=O)\) is due to adventitious carbonate.

<table>
<thead>
<tr>
<th>Mg:Al</th>
<th>(\nu(OH))</th>
<th>(\delta(OH))</th>
<th>(\nu(CN))</th>
<th>(\delta(MCN))</th>
<th>(\nu(C=O))</th>
<th>lattice peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>3625, 3468</td>
<td>1635</td>
<td>2034, 2045(sh)</td>
<td>586</td>
<td>N. O.</td>
<td>668, 449</td>
</tr>
<tr>
<td>3:1</td>
<td>3646(sh), 3468</td>
<td>1642</td>
<td>2086, 2032, 2045(sh)</td>
<td>1372</td>
<td>586, 414</td>
<td></td>
</tr>
</tbody>
</table>
Figure 12. Full-scale FTIR spectra of (I) 2:1 and (II) 3:1 Mg:Al LDH ferrocyanide.
Presence of High Frequency OH Bands

The presence of non-hydrogen-bonded OH groups in LDHs intercalated with ML₆-type anions is expected as a geometric consequence of the interaction of such anions with the hydroxide layers. High frequency hydroxide stretches attributable to such groups are clearly resolved in conventional spectra of 2:1 LDH ferrocyanide and in oriented LDH ferricyanide samples. The high frequency $\nu$(OH) is clearly seen near 3640 cm⁻¹ in Figure 12(I). (One might be tempted to assign this peak to brucite (Mg(OH)₂) present in the solid, but our own experiments and published literature indicate that brucite exhibits its sharp peak ~3700 cm⁻¹.) We have observed similar high frequency $\nu$(OH) peaks in 2:1 Mg:Al LDH nickelocyanide and oriented samples of 2:1 Mg:Al LDH ferricyanide but not in non-oriented 3:1 Mg:Al LDH ferrocyanide, 2:1 Mg:Al LDH ferricyanide, or 3:1 Mg:Al LDH nickelocyanide. The exact origin of these high frequency OH bands is, as yet, unknown.

Chemical Interaction with Ferricyanide

Figures 9 and 10 represent the conventional and oriented FTIR spectra of 2:1 and 3:1 Mg:Al LDH chloride treated with aqueous potassium ferricyanide. As previously discussed, we attribute the near-symmetric peaks having a maximum absorbance ~ 2112 cm⁻¹ to intercalated ferricyanide. We always observe a secondary peak near 2040 cm⁻¹ when we make this material. The structure of this peak, and its behavior under orientation, clearly indicate that it is identical with intercalated ferrocyanide. Idemura observed similar behavior from LDH-ferricyanide systems. It is likely that cyanide itself acts as the reducing agent in this particular system.

Chemical Interaction with Ferrocyanide

Figures 11 through 13 depict the FTIR spectra and powder XRD patterns for the product of treatment of Mg:Al LDH chloride with potassium ferrocyanide. Both sets of data are indicative of a well-ordered, single-phase LDH; namely Mg:Al LDH ferrocyanide. We will refer to this material (having a basal spacing of ~10.9 Å, a split ν(CN) peak with maximum absorption near 2035 cm⁻¹, a high frequency ν(OH) (~3640 cm⁻¹, not Mg(OH)₂), and a characteristic LDH lattice vibration ~450 cm⁻¹) as LDH.
ferrocyanide and its component ferrocyanide as “intercalated” ferrocyanide. In our normal exchange procedures, used to prepare LDH ferrocyanide, we only see “intercalated” ferrocyanide. There have been several reports\textsuperscript{21-23} in the literature of ferrocyanide oxidizing to ferricyanide upon intercalation into LDH, largely based upon the appearance of a second $\nu$(CN) band near 2085 cm\textsuperscript{-1}. Our infrared evidence does not support such a claim. As previously stated, intercalated ferricyanide shows a $\nu$(CN) maximum near 2112 cm\textsuperscript{-1}, very much like the aqueous anion.

\textbf{Figure 13.} Expanded-scale FTIR spectra, conventional (upper) and oriented (lower) of (a) 2:1 and (b) 3:1 Mg:Al LDH ferrocyanide.
Figures 14 and 15 show the FTIR spectra and powder XRD patterns for the cubic ferrocyanide species K$_2$MgFe(CN)$_6$ and (NH$_4$)$_2$MgFe(CN)$_6$. The infrared spectra show ν(CN) absorptions of ~2088 cm$^{-1}$ for the potassium species and ~2085 cm$^{-1}$ for the ammonium species. Other absorptions of interest include the NH stretching and bending vibrations for the ammonium material and M-C stretches and M-C-N bends for both compounds. Significant infrared absorptions are listed, along with their assignments, in Table 12. Table 13 lists our observed XRD data for these cubic materials along with literature values. Our data are completely consistent with a cubic structure, as commonly found$^{64}$ for M(I)$_2$M(II) ferrocyanides.

![Figure 14. FTIR spectra of (I) K$_2$MgFe(CN)$_6$ and (II) (NH$_4$)$_2$MgFe(CN)$_6$.](image-url)

50
Figure 15. Powder XRD patterns of (a) $K_2\text{MgFe(CN)}_6$ and (b) $(\text{NH}_4)_2\text{MgFe(CN)}_6$. 
Table 12. FTIR data (all values in cm$^{-1}$) for $M_2$MgFe(CN)$_6$, where $M = K^+$ or NH$_4^+$.

<table>
<thead>
<tr>
<th></th>
<th>$\nu$(NH)</th>
<th>$\nu$(CN)</th>
<th>$\delta$(OH)</th>
<th>$\delta$(NH)</th>
<th>$\delta$(MCN)</th>
<th>$\nu$(MC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>2083</td>
<td>1619</td>
<td>-----</td>
<td>597</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3234</td>
<td>2082</td>
<td>1652</td>
<td>1417</td>
<td>600</td>
<td>477</td>
</tr>
</tbody>
</table>

Table 13. Powder XRD data ($d$-spacings given in Å) for $M_2$MgFe(CN)$_6$. Literature values, given in parentheses, are from reference 32.

<table>
<thead>
<tr>
<th>hkl</th>
<th>$K_2$MgFe(CN)$_6$</th>
<th>(NH$_4$)$_2$MgFe(CN)$_6$</th>
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<tr>
<td>111</td>
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<td>5.096 (5.146)</td>
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<td>210</td>
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<td>220</td>
<td>3.635 (3.645)</td>
<td>3.611 (3.627)</td>
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<tr>
<td>212</td>
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</tr>
<tr>
<td>311</td>
<td>-----</td>
<td>3.080 (3.087)</td>
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<tr>
<td>222</td>
<td>3.069 (3.053)</td>
<td>2.956 (2.951)</td>
</tr>
<tr>
<td>320</td>
<td>2.859 (2.858)</td>
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</tr>
<tr>
<td>321</td>
<td>2.790 (2.789)</td>
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</tr>
<tr>
<td>321</td>
<td>-----</td>
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<td>2.552 (2.557)</td>
</tr>
<tr>
<td>322</td>
<td>2.515 (2.534)</td>
<td>-----</td>
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<tr>
<td>410</td>
<td>2.439 (2.499)</td>
<td>-----</td>
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<tr>
<td>331</td>
<td>-----</td>
<td>2.345 (2.345)</td>
</tr>
<tr>
<td>420</td>
<td>-----</td>
<td>2.292 (2.287)</td>
</tr>
</tbody>
</table>

We then decided to treat 2:1 Mg:Al LDH with ammonium ferrocyanide. Figure 16 shows the infrared spectrum and powder XRD pattern for the product of that reaction. The infrared spectrum shows features from both Mg:Al LDH ferrocyanide and ammonium magnesium ferrocyanide. The $\nu$(CN) region shows two well-defined peaks; one having a maximum absorbance $\sim$2035 cm$^{-1}$ and the characteristic shape of
intercalated ferrocyanide within 2:1 Mg:Al LDH, and the other a symmetric peak with a maximum near 2088 cm$^{-1}$, very similar to the ammonium magnesium ferrocyanide. The region between 3600-2500 cm$^{-1}$ shows $\nu$(OH) stretches $\sim$3500 and 3640 cm$^{-1}$ corresponding to the usual LDH OH stretch and the previously discussed high-frequency peak found in LDH metallocyanides as well as peaks near 2800 cm$^{-1}$ characteristic of $\nu$(NH) in ammonium magnesium ferrocyanide. The XRD pattern (Figure 16b) also supports our claim of a two-phase system. The diffraction pattern is dominated by peaks from the highly symmetric cubic species, but peaks are also seen that exactly match the $d_{003}$ and $d_{006}$ reflections for LDH ferrocyanide.

Figure 16. FTIR spectrum (a) and powder XRD pattern (b) of product obtained by treating 2:1 Mg:Al LDH chloride with ammonium ferrocyanide.
As previously stated, in our hands, treatment of LDH with potassium ferrocyanide usually yields only intercalated ferrocyanide. We have, however, shown that more of the “reacted” ferrocyanide species is formed if the exchange reaction is carried out at lower pH.\(^6\)\(^5\) Additionally, those literature preparations described as leading to the 2085 cm\(^{-1}\) species involved either low stated pH\(\text{22}\) or direct contact of a soluble magnesium (or zinc) salt and potassium ferrocyanide solutions.\(\text{21}\) In the former case, our own pH studies\(\text{59}\) indicate that at pH values below \(\sim\)7.5, the Mg:Al LDH would be expected to partially dissolve yielding free magnesium ions (which could then form potassium magnesium ferrocyanide) and either Al(OH)\(_3\) or an aluminum-rich LDH phase. Cubic material would be expected to form in these cases in the same manner as in our direct reaction of magnesium ions with ferrocyanides.

We thus suggest that the two different v(CN) peaks sometimes observed in LDH ferrocyanide are caused by ferrocyanide existing in two different environments; one intercalated and the other reacted to form cubic materials, for the following reasons:

1. Potassium magnesium ferrocyanide and ammonium magnesium ferrocyanide are cubic (or near cubic) materials. Cubic ferrocyanides of this type generally show v(CN) absorptions near 2085 cm\(^{-1}\).\(^5\)\(^8\) Specifically for potassium magnesium ferrocyanide and ammonium magnesium ferrocyanide, our infrared investigations show v(CN) stretches at 2083 cm\(^{-1}\).

2. Mg:Al LDH, upon exposure to excess ammonium ferrocyanide solution, develops two v(CN) peaks; one at 2035 cm\(^{-1}\), expected for hydrogen-bonded, intercalated ferrocyanide, and the other near 2085 cm\(^{-1}\). The 2085 cm\(^{-1}\) peak shows no effect from sample orientation, consistent with its cubic nature. Intercalated ferricyanide, by contrast, exhibits its v(CN) stretch near 2112 cm\(^{-1}\), and shows a detectable, if small, orientation effect.

3. Mg:Al LDH, upon exposure to excess ammonium ferrocyanide solution, develops two sets of X-ray diffractions; one corresponding to LDH ferrocyanide and the other to ammonium magnesium ferrocyanide.

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4. The published work\textsuperscript{22} leading to the formation of the 2085 cm\textsuperscript{-1} species involved reaction conditions expected to provide free magnesium ions in contact with dissolved potassium ferrocyanide.

We have also treated zinc-containing LDH (both Zn:Al and Zn:Cr) with ferrocyanide solution, and found that these materials form cubic zinc ferrocyanide much more readily than their Mg-containing counterparts. In LDH containing zinc, appreciable amounts of cubic ferrocyanide are seen in the infrared spectra of materials obtained by treatment of the LDH with potassium ferrocyanide at room temperature. Our infrared spectra for such zinc-containing materials are consistent with those reported in the literature for similar Zn:Al materials.\textsuperscript{21}

The reactions between Mg:Al LDH and either ferrocyanide or ferricyanide provide some interesting, and hopefully exploitable, chemistry. In both cases, most of the anion ends up as intercalated species within the layered system. During ferricyanide intercalation, some of the ferricyanide is reduced to ferrocyanide, which also intercalates into the LDH. Treatment of LDH with ferrocyanide provides perhaps the most exciting chemical possibilities. When Mg:Al LDH is exposed to a solution of ferrocyanide at a reduced pH (either by addition of acid or use of ammonium ferrocyanide), varying amounts of cubic ferrocyanides are formed. Such a situation presents the possibility of having ferrocyanide in any of three distinct environments; intercalated into the LDH interlayer, adsorbed\textsuperscript{66} onto the outer surface of the LDH,\textsuperscript{67} or in a cubic material. Such varied environments suggest the possibility of varied chemistry as well. The formation of ammonium magnesium ferrocyanide from the treatment of Mg:Al LDH with ammonium ferrocyanide is particularly exciting in connection to the origins of life because it presents a method for concentrating cyanide and ammonia in the same, easily-formed, insoluble substance. However, our general method of preparing ferrocyanide-intercalated LDH, which we present here, provides a method which limits this conversion to cubic ferrocyanide in those cases where a pure LDH ferrocyanide is required.
From “Cyanide Self-Addition, Controlled Adsorption, and Other Processes at Layered Double Hydroxides” published in Origins of Life and Evolution of the Biosphere vol. 31, no. 1 of 2 (2001), pages 53-69. Collaborative effort with Joseph W. Bocclair, Paul S. Braterman, Jianping Jiang, Shaowei Lou, Zhiming Wang and Faith Yarberry. All cyanide intercalation experiments were performed by the author, except for some additional intercalations of 3:1 material and experiments involving $^{13}$C-labeled cyanide, which were performed by Joseph W. Bocclair. HPLC analysis and kinetic studies were also performed by Joseph W. Bocclair; GAP reactions were performed by Faith Yarberry. IR data for all compounds were taken from previously published works, along with the data relating to LDH carbonates. Extreme care was taken in the preparation of these compounds; the following paper contains detailed information on their synthesis, but for descriptions of the starting materials, the reader should refer back to the Introduction at the start of this Part II.

Abstract

Layered double hydroxides (LDH) are anion-exchanging materials of the type \[ \text{M(III)M(II)}_x(\text{OH})_{(2x+2)}Y \] that occur abundantly in nature, and can concentrate, protect, and activate simple organic anionic species of possible relevance to the earliest organisms. We now wish to report progress in the following areas:

1. Internal vs. external uptake of anions. Ferrocyanide does not displace carbonate from synthetic hydrotalcite (Mg:Al LDH carbonate) but is nevertheless taken up on the outside of the particles. In other cases, anion uptake is controlled by specific hydrogen bonding requirements rather than by charge density alone, a feature that can be used to control whether uptake will be both internal and external, or external only. These two findings taken together have important implications for specific catalysis by LDH, since specific hydrogen bonding will affect the individual and relative conformations of substrate anions, and anions occupying space in the interlayer will be under tighter constraints than those adsorbed externally.

2. Specific reactions catalyzed by LDH. We have found that the LDH \[ \text{Mg}_2\text{Al(OH)}_6\text{Cl} \] catalyzes the self-addition of cyanide, to give in a one-pot reaction at low concentrations an increased yield of diaminomaleonitrile and in addition, at higher
concentrations, a purple-pink material that adheres to the LDH. We are investigating whether this reaction also occurs with hydrotalcite itself, what is the minimum effective concentration of cyanide, and what can be learned about the products and how they compare with those reported at high HCN concentrations in the absence of catalyst.

Introduction

Both strong and weak roles have been suggested for inorganics in the origins of life. According to the weak role theory, inorganics may have functioned as a source of order, through concentration and catalysis, without necessarily using anything more sophisticated than the highly redundant information of their lattice structures. According to the strong role theory, Darwinian evolution began with the selective elaboration of information embodied in the lattice variations of inorganic materials, with subsequent genetic takeover by organics. The strong role theory requires that inorganics should also be able to meet the requirements of the weak role theory, but not necessarily vice versa. It is therefore important, without at this stage attempting to distinguish between strong and weak roles, to establish how generally inorganic materials can play the required role of directing reactions of simple precursors towards the formation of more interesting materials.

Which inorganics should be selected for study, out of the enormous number available? Model materials (i.e. those whose behavior can give us insight into the processes leading to the origins of life) would have the ability to concentrate prebiotics of interest, most of which are anionic or polar, and hydrogen-bonding. Candidate materials (i.e. those that, as a matter of historical fact, may have actually played a part in these processes) would in addition have been readily available on the early Earth.

For these reasons, we and others have concentrated our attentions on the layered double hydroxides (LDH), formed in nature by the weathering of basalts or by precipitation from saline lakes. These materials have been reviewed in the context of the origins of life by Kuma et al., and more generally by several authors. They have the general formula M(II)$_x$M(III)(OH)$_{(2x+2)}$Y, where, in present-day minerals, M(III) is most commonly Fe or Al, and M(II) is most commonly magnesium (often with partial
inclusion of Mn and/or Fe). Nowadays, the anion Y may be \( \frac{1}{2}\text{CO}_3 \), Cl, or \( \frac{1}{2}\text{SO}_4 \), although this last may not have been available on the early Earth. The schematic structure is shown in Figure 1; each metal ion being surrounded by six hydroxides, and each hydroxide by three metal ions, while the interlayer anion Y, and interlayer water, occupy space between the close-packed metal hydroxide layers. Note that interlayer hydroxide has no free lone pairs, so that it cannot function as a base without disrupting the lattice. Despite this, LDH are known to act as basic catalysts (see for example Pinnavaia et al., 1995), perhaps because of incorporation of hydroxide or carbonate into the interlayer space. This OH group does, however, have a pendant hydrogen, which can take part in H-bonding to interlayer water, thus enhancing its acidity. LDH provide a specific, orderly, strongly hydrogen-bonding environment. LDH can readily be prepared in the laboratory, with the prospect of controlling their behavior by varying the layer charge density, the identity of M(II), M(III), Y; the particle size and degree of structural perfection and ordering, and whether reaction occurs on external surfaces, or the interlayer space.

**Scope of this paper**

In this paper, we make three claims for layered double hydroxides: (1) that they provide specific H-bonding environments for adsorbed anions; (2) that they can adsorb anions onto both internal and external surfaces, with perhaps different results; and (3) that they can catalyze reactions leading to molecules of possible biological interest. These reactions include aldol additions using glycolaldehyde phosphate, and, as we now report, the catalytic self-addition of cyanide.

**Experimental**

HPLC-grade methanol (Aldrich) was used in all chromatography. The glycolaldehyde phosphate (GAP) reaction was performed using ~30 mL of a 3mM solution of GAP provided by Dr. G. Arrhenius at UCSD.

Magnesium aluminum LDH \([\text{Mg}_2\text{Al(OH)}_6\text{Cl}] \text{ and } \text{Mg}_3\text{Al(OH)}_8\text{Cl}\) were prepared using previously described methods, using excess Mg\(^{2+}\) to increase reproducibility, and to minimize the incorporation of unwanted interlayer carbonate or hydroxide, by buffering the pH. Generally, Mg\(_2\)Al(OH)\(_6\)Cl was prepared by gravimetrically titrating a solution
0.3M in MgCl₂, 0.1M NaCl (to achieve an overall 1.0M concentration of Cl⁻), and 0.1M in AlCl₃ with sufficient 50% NaOH (separately standardized; this material was used because of its low carbonate content, since sodium carbonate precipitates out) to achieve a hydroxide to aluminum ratio of 6:1. The pH of the suspensions was regularly monitored and the stoichiometry further confirmed by reference to the equivalence point for the initial precipitation of Al(OH)₃. The whole process was carried out under a slow stream of nitrogen. Following the addition of base, the whole suspension was refluxed overnight, also under nitrogen. The materials were collected and washed via centrifuge and handled as damp pastes. Similarly, Mg₅Al(OH)₈Cl was prepared from a solution with initial Mg²⁺ and Al³⁺ concentrations of 0.4 and 0.1 M respectively. The excess Mg²⁺ is present to prevent the pH of the solution from varying very far from the precipitation pH for the LDH. Exchange reactions were performed by suspending a sample of LDH in 50 mL of a solution 0.1M in either potassium ferrocyanide or potassium hexacyanoplatisate(IV) and magnetically stirring overnight. For the GAP reaction, a small sample of 2:1 LDH was suspended in the supplied 3 mM GAP solution and allowed to stir overnight. All exchange reactions were performed under a sealed, nitrogen atmosphere. For reactions between LDH and KCN, solutions were prepared to be ~ 0.04M in LDH chloride with concentrations of KCN ranging from 0.05M to 4M. The 0.05M KCN reactions were run in a three-necked round-bottom 250 mL flask fitted with a stopcock which allowed sampling of the reaction mixture without compromising the nitrogen atmosphere.

FTIR and powder XRD data were collected as in earlier work. HPLC data were collected using a Waters 501 pump connected to a Waters 996 photodiode array detector collecting from 210 to 400 nm with Millenium™ 32 software. The column was a Phenomenex Columbus 5μ C8 100 Å and the mobile phase was a 50 : 50 mixture of HPLC grade methanol (obtained from Aldrich) and water (buffered at pH = 6.0 by a 20 mM sodium hydrogen phosphate / disodium hydrogen phosphate buffer).

A note of caution. Initially, when we were collecting our HPLC data, we observed a peak of varying intensity which exhibited a benzenoid spectrum. The origin of this peak was eventually traced to a residue from rubber stoppers which we were using at the time. Since this discovery, we have ceased to use such septa in our reactions, have
used only Dow Corning silicone grease to seal ground glass joints, and have run blanks of our operating systems to eliminate the possibility of contaminants.

Results and Discussion

Claim (1) is simply established by close examination of the ν(CN) mode of [Fe(CN)$_6$]$^{4-}$, which is sensitive to its exact H-bonding environment, when this anion is incorporated into LDH (Figure 17). As this Figure shows, in high charge density LDH (Mg:Al = 2:1), all the ferrocyanides are in the same environment, the splitting of the ν(CN) mode being due$^{30}$ to the fact that the local symmetry is now D$_{3d}$, as opposed to O$_h$ in the free anion. When the LDH charge density is lowered (Mg:Al=3:1), the splitting pattern is reversed, indicating a significant change in the dynamic interaction between CN and OH groups, while the appearance of several minor peaks implies the existence of a range of different possible environments.

![Figure 17. Conventional (upper) and in-plane oriented (lower) FTIR spectra in the ν(CN) region of 2:1 (a) and 3:1 (b) Mg:Al LDH ferrocyanide.](image)
Furthermore, we have very recently found that specific H-bonding influences the type of species that can be taken up by LDH, as well as their exact environment. Thus the anion [Pt(CN)$_6$]$^{2-}$ can be quantitatively incorporated into LDH with Mg:Al=4:1, but not 3:1, implying that this anion requires more space than would be predicted on simple charge density arguments, or even after consideration of the need for a sufficient number of pendant OH groups to bond to CN. These facts suggest the existence of additional constraints, such as, perhaps, a tendency to avoid situations where adjacent pendant OH groups are involved in H-bonding. Such constraints will undoubtedly affect the uptake and orientation of polar prebiotic anions by LDH. These differences in interlayer anion environment may well lead to varied chemical behavior of LDH based on changing cation layer charge density, with implications for subsequent prebiotic reactions using such minerals.

*Claim (2)* has already been established, in the case of ferrocyanide, by our finding that this anion is detectable by IR but not by XRD in the material obtained when [Mg$_2$Al(OH)$_6$]$_2$CO$_3$ is exposed to this anion in solution, showing that it is taken up on the outside (but not inside) surface of the solid, while other workers have independently established that under these conditions the externally adsorbed ferrocyanide forms a two-dimensional superlattice. LDH intercalated with carbonate are the most abundant mineral samples and also very likely to have existed under presumed early Earth conditions. This result is significant because it allows a method for concentration of ferrocyanide (or other anions of interest) from solution by these common, naturally-occurring minerals.

We now report that, although glycolaldehyde phosphate (GAP), like ferrocyanide, is known to be readily displaced by carbonate from the interlayer position in LDH, difference spectra show that when [Mg$_2$Al(OH)$_6$]$_2$CO$_3$ is exposed to a 3 mM solution of GAP [gift of Dr G. Arrhenius], the GAP is adsorbed onto (presumably) the external surfaces of the mineral (Figure 18). This finding could have significant implications in prebiotic chemistry. Formaldehyde, being neutral, is not taken up as such into LDH, and
yields of pentose from the LDH-catalyzed reaction of interlayer GAP in the presence of formaldehyde are small (~5%). Presumably, in this work, the favored reaction was the self-addition of GAP within the interlayer, where formaldehyde cannot follow. The LDH-catalyzed self-addition of formaldehyde has been demonstrated by Mizutani and coworkers together with hydrogen transfer, albeit at high concentrations and temperatures; it is not known whether this process occurs on the LDH surface, or whether some incorporation of occurring de into the interlattice space occurs under these conditions. It therefore seems to us important to explore the interaction of formaldehyde with externally adsorbed GAP on [Mg₂Al(OH)₆]₂CO₃. This could provide a pathway for
the LDH-directed formation of sugars from dissolved formaldehyde, even though formaldehyde (unlike GAP) is not adsorbed internally to any detectable extent by the LDH. Externally adsorbed GAP is available to interact with solution species, as internally adsorbed material is not; and reactions involving LDH carbonate are of special interest because it is (and presumably was) the most common mineral of its class. Addition to an already anchored chain is expected on general grounds\textsuperscript{71} to incur a smaller entropy penalty than formation of a new chain. Externally adsorbed GAP on this material must be subject to important constraints [Claim (1), above], with possible implications for the successive additions of formaldehyde, and experimental investigations of this system are pending.

Claim (3) has already been established, for aldol type addition reactions, by the work cited above, with possible implications for the formation of carbon-carbon bonds in general and sugars in particular We now report that LDH can, in addition, promote the self-addition reaction of cyanide, with possible implications for the formation of a range of interesting molecules, ranging from amino acids to purines and pyrimidines.

While the self-addition reaction of cyanide has a special place in classical prebiotic chemistry,\textsuperscript{50,51,53} it has been recognized for more than 30 years that under normal circumstances this reaction will not be productive at low cyanide concentrations, because under such conditions hydrolysis to give formamide (first order in cyanide) competes successfully with the desired self-addition (second order in total cyanide).\textsuperscript{72,73} It would therefore be extremely helpful to find conditions under which the self-addition reaction is catalyzed at low cyanide concentrations. Ferris et al.\textsuperscript{74,75} have investigated the behavior of cyanide in the presence of montmorillonite clays, but find that the main effect is to accelerate the unwanted oxidation of DAMN to diiminosuccinonitrile (DISN), thus effectively removing one significant product of the cyanide self-addition. We have investigated the behavior of cyanide in the presence of LDH (specifically, 2:1 or 3:1 Mg:Al LDH, initially in the form of chloride), and now report acceleration of the self-addition reaction under low concentration conditions, with disappearance of cyanide, and formation of diaminomaleonitrile, other as yet unidentified materials, and, at higher concentrations, pink to purple material that appears to be strongly associated with the LDH.[7]
The uncatalyzed tetramerization of HCN has been shown to proceed through the mechanism shown in Figure 19. Sanchez et al.\textsuperscript{72} reported that the rate-determining step in this reaction is the addition of CN\textsuperscript{-} to HCN, giving the rate law

\[
\frac{d[\text{tetramer}]}{dt} = k [\text{CN}^-] [\text{HCN}]
\]

with values of 0.096 liter mole\textsuperscript{-1} day\textsuperscript{-1} and 0.0032 liter mole\textsuperscript{-1} day\textsuperscript{-1} for 40°C and 10°C respectively. Thus, the polymerization is expected to proceed at maximum velocity near the pK\textsubscript{a} of HCN which is 9.2, and is in direct competition with the simple hydrolysis reaction, which is dominant at low concentrations.

In the presence of 2:1 Mg:Al LDH chloride (~0.04 equivalents/L), solutions of KCN ([CN\textsuperscript{-}] ≥ 0.1M) react to form the cyanide tetramer diaminomaleonitrile (DAMN) and other, as yet unidentified, products including, within 24 hours, the aforementioned pink / purple species. Figure 20 shows an HPLC chromatogram for a 0.8M KCN solution stirred in the presence of 2:1 Mg:Al LDH chloride for approximately 1 week. These data show a number of products being formed in addition to DAMN at these high concentrations. These solutions, with added LDH, show initial pH values in the range of 10 – 10.5. Following reaction times of greater than one day, the pH of these solutions gradually increases toward values above 12. This rise in pH is inevitable for formation of HCN polymer (or any overall neutral species) from anionic cyanide.
Figure 20a. HPLC chromatogram at 293 nm for 0.8 M KCN solution in the presence of 2:1 Mg:Al LDH chloride (reaction time ~7 days, pH ~ 10.8). Numbers correspond to retention times in minutes.

In the presence of 3:1 Mg:Al LDH chloride, (~0.04 equivalents/L), slightly more concentrated solutions of KCN ([CN\(^-\)] \geq 0.1M) react to form DAMN in amounts greater than in the absence of LDH, but generally in amount less than in the presence of 2:1 Mg:Al LDH chloride. No detectable amounts of DAMN were seen in experiments where 3:1 LDH was treated with 0.05M KCN. It would also appear that in the case of 3:1 Mg:Al LDH, the LDH-promoted oligomerization of cyanide stops at the tetramer since we have seen no evidence for formation of the colored material seen in the 2:1 LDH case. We attribute this difference in reactivity to the greater distance between the charge centers in 3:1 LDH.
Figure 20b. HPLC UV-Vis spectra for selected components for 0.8M KCN solution in the presence of 2:1 Mg:Al LDH chloride (reaction time, ~7 days, pH ~10.8). Numbers correspond to retention times in minutes.

Figure 21 illustrates the observed formation of DAMN from 0.1M KCN solutions both in the presence and absence of Mg:Al LDH. This plot clearly shows the effect of LDH on the production of DAMN. In the presence of 2:1 Mg:Al LDH chloride, the concentration of DAMN in solution reaches a maximum value near 150 hours. Following this time, the DAMN concentration decreases, showing that the DAMN is being used in some other process. In the presence of 3:1 LDH, the DAMN concentration continues to increase for at least 6 days. The lack of consumption of DAMN and the lack of formation of a significant amount of dark material leads us to suggest that the consumption of DAMN in the 2:1 case is related to formation of the dark material. The maximum concentration of DAMN in solution in the presence of 2:1 LDH was 1.9 mM,
occurring at 6 days. This corresponds to a 0.008% conversion of cyanide to DAMN. Allowing the reaction to continue past this point causes the DAMN concentration to drop to 1.2 mM after nearly 10 days. After 7 days, the DAMN concentrations for experiments having 2:1 LDH, 3:1 LDH, and no LDH were 1.64 mM (0.0065% conversion), 1.1 mM (0.0044% conversion), and 0.29 mM (0.0012% conversion) respectively. Table 14 summarizes the data for the average rates of DAMN formation over different time intervals for this series of reactions.

![Graph of DAMN production with trend lines](image)

**Figure 21.** Comparison of production of diaminomaleonitrile from 0.1M KCN solutions in both the presence of 2:1 and 3:1 Mg:Al LDH chloride and the absence of LDH. Trend lines added to guide the eye.

**Table 14.** Concentration of diaminomaleonitrile from 0.1M KCN solutions (solution p\(\text{H} = 10.5\)). Concentrations of DAMN are given in \(\mu\text{M}\).

<table>
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<th>Time (days)</th>
<th>3:1 LDH present</th>
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</tbody>
</table>
More dilute solutions (0.05M) of KCN in the presence of ~0.04M LDH chloride generally show pH values near 9.8. In order to clearly assess the effect of LDH on cyanide self-addition we performed parallel experiments in which 0.05M KCN solutions were stirred both in the presence and absence of 2:1 Mg:Al LDH. The experiment without LDH was buffered at pH 9.8 by a carbonate/bicarbonate buffer. Figure 22 illustrates the formation of the HCN tetramer from 0.05M KCN solutions at this pH both in the presence of 2:1 Mg:Al LDH chloride, as well as the absence of LDH. The DAMN concentration after 9 days in the experiment with LDH is equal to 15 μM for the 2:1 material, corresponding to ~ 0.12 % conversion of HCN to the tetramer, while the parallel reaction in the absence of LDH showed a DAMN concentration of 0.3 μM (0.002 % conversion). At the end of the nine day reaction period, the 2:1 LDH began to show a light yellow-brown discoloration; indicative of formation of adsorbed material, while the 3:1 material remained colorless. By comparison, Sanchez et al. found 0.1% conversion to the tetramer over three days in 0.01M HCN solutions under eutectic conditions (0.01M KCN/0.005M NH₃, -22°C, 3 days). In Table 15, we report average rates of DAMN formation over different time intervals. The production of the HCN tetramer varies between 0.5 mM/day to nearly 2 mM/day. Generally, the average production of DAMN seems to be fairly constant through 5 days at which point, the average rates decrease somewhat. Thus the initial build-up of DAMN is followed by its loss, perhaps by hydrolysis or by conversion to the dark material. In order to examine further the effect of LDH on promoting the cyanide self-addition, we exposed a 0.01M KCN solution to a sample of 2:1 Mg:Al LDH chloride. Following a reaction period of four days, the solution pH was 9.6 and the concentration of DAMN in solution was found to be 0.27 μM. Such a concentration constitutes nearly twice as much DAMN in solution as we observe after six days in 0.05M KCN solutions with no LDH present, and (assuming the uncatalyzed reaction remains second order) implies an increase in rate, due to the LDH, by a factor of around 50.
Table 15. Concentration of diaminomaleonitrile from 0.05 M KCN solutions (solution pH = 9.8°). Concentrations of DAMN are given in μM.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>LDH not present</th>
<th>2:1 LDH present</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.063</td>
<td>Not Detected</td>
<td>0.038</td>
</tr>
<tr>
<td>0.167</td>
<td>Not Detected</td>
<td>0.087</td>
</tr>
<tr>
<td>1.04</td>
<td>Not Detected</td>
<td>1.5</td>
</tr>
<tr>
<td>2.00</td>
<td>Not Detected</td>
<td>6.4</td>
</tr>
<tr>
<td>4.00</td>
<td>Not Detected</td>
<td>8.1</td>
</tr>
<tr>
<td>6.00</td>
<td>0.14</td>
<td>8.0</td>
</tr>
<tr>
<td>12.00</td>
<td>0.27</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 22. Comparison of production of diaminomaleonitrile from 0.05 M KCN solutions in both the presence and absence of 2:1 Mg:Al LDH chloride. Trend lines added to guide the eye.
We have performed additional, cursory experiments on the interaction between cyanide and 2:1 Mg:Al LDH carbonate. Treating the LDH carbonate with concentrated KCN solutions (0.2 M) results in no visible formation of the purple-pink material. This is in direct contrast to similar experiments with LDH chloride where the oligomeric material appears overnight. Furthermore, treatment of 2:1 Mg:Al LDH carbonate with 0.1M KCN results in no discernible formation of DAMN. These results strongly suggest that the oligomerization of cyanide occurs in the interlayer of the LDH.

In summary, we have found that the LDH Mg₂Al(OH)₆Cl catalyzes a novel self-addition of cyanide, to give among other products, in a one-pot reaction, a purple-pink material that adheres to the LDH. We are investigating the effects of working at even lower concentrations, and the nature of the products. We conclude at this stage that:

1. 2:1 LDH catalyze (and possibly modify) the self-addition reaction of cyanide.
2. Various species are formed in detectable amounts, in addition to DAMN.
3. Pink and purple materials (presumably, conjugated CN-containing substances) are formed at higher cyanide concentration. These are insoluble in water but more or less firmly attached to LDH.
4. 3:1 LDH catalyze production of DAMN from cyanide solutions, but do not lead to the formation of the pink and purple materials seen with 2:1 LDH.

**Perspective:** Our results extend the range of reactions of prebiotic interest in which LDH can catalyze and direct reactions involving active [as well as activated] species. At the least, such reactions using inorganic materials should be part of the armory for the "prebiotic" synthesis of molecules relevant to present-day biochemistry. More usefully, perhaps, such reactions may give us clues as to what actual processes and molecules were available for the very earliest stages of carbon-based terrestrial life. Finally, we would suggest that, if there ever in fact was an inorganics-to-organics genetic takeover, it would presumably have involved specific catalysis and direction, by the inorganic materials, of such simple organic reactions.
COMMENTARY

“Likewise the IR data of cobalticyanide reported here are indeed virtually identical in aqueous and intercalated environments, showing ν(CN) values of 2128 cm⁻¹ and 2127 cm⁻¹ for the intercalated and aqueous species, respectively.”
Comment: This shows how truly weakly held some complexes are in LDH systems; stronger H-bonding interactions with the layers would appear as a larger shift in the IR spectrum of the ν(CN) toward a lower wavenumber on intercalation. The cobalticyanide anion seems, in this case, not really to be held by the LDH at all, save for the very small interaction which causes a 1 cm⁻¹ shift in the IR. Other systems show larger shifts on intercalation (square-planer M-CN complexes come to mind) and indicate stronger interactions with the LDH layers.

[21] On the Cobalticyanide/Nitroprusside paper: Results section, 1st paragraph after Deformation of Intercalated Cobalticyanide, last sentence. “We suggest this behavior is due to the three-minus cobalticyanide forming weaker hydrogen bonds with the layer than the four-minus ferrocyanide.”
Comment: After some thought, I think that this phenomenon may be strongly influenced by the charge on the central atom. The Fe in ferrocyanide is Fe²⁺ while the Co in cobalticyanide is Co³⁺, making the radius of the Co³⁺ significantly smaller than its iron counterpart and increasing the rigidity of [Co(CN)₆]³⁻ relative to [Fe(CN)₆]⁴⁻. This affects the ν(CN) by not allowing intercalation to change the M-CN bond distance (which would imply increased π-backbonding interactions) with Co³⁺ as much as with Fe²⁺, and thus we see less change in the ν(CN) of the cobalticyanide than with the ferrocyanide when they are intercalated into a LDH. If true, this phenomenon should also show up in the case of intercalated ferricyanide; indeed, the two anions exhibit very similar behavior relative to ferrocyanide. In all likelihood this is merely a different way to explain the same reasoning used already, but there are at least some subtle differences. I can think of no satisfactory method to determine which theory is more accurate other than Occam’s Razor, which eliminates this more complex explanation in favor of the simpler one.
[31]. On Ruthenocyanide paper: Conclusions section. “We have demonstrated that the ruthenocyanide anion behaves in a manner completely analogous to the ferrocyanide anion under the same conditions.”

Comment: One notable exception is the lack of formation of “cubic material” which can often occur, presumably as a result of mechanical stress during IR sample preparation using KBr discs. To my knowledge, I am the only person who has taken the IR spectrum of an LDH ruthenocyanide; having never taken the IR spectrum of a LDH ferrocyanide system, I cannot say for certain whether this lack of ruthenium “cubic material” is due to differences in preparation techniques or not.

[41]. On the square-planar note: Results section. “The powder X-Ray diffraction patterns for 2:1 Mg:Al LDH [Ni(CN)₄]²⁻ shows d₀₀₃ and d₀₀₆ reflections at 11.05 and 5.60 Å, respectively.”

Comment: This is the normal spacing for the interlayer gallery height (11.05 Å) after intercalation of [Ni(CN)₄]²⁻. A second reflection occurs at half height (5.60 Å) and is consistent with “2nd harmonic” reflection. Interestingly, a later elemental analysis showed that the ratio of N to Ni was closer to 5:1 than the expected 4:1 for [Ni(CN)₄]²⁻. The anion sits at an angle of ~75° to the lattice because it is actually pentacyanonickelate(II), rather than the original tetracyanonickelate(II) species. The reasons for this unexpected behavior are still unclear; no other nickel-containing species have been found in either the LDH or the mother liquor.

Questions: Are there any Ni-containing compounds that are blue? Isn’t an Al-Ni(CN)₄ compound significantly less thermodynamically stable than a 2:1 LDH? Is [Al(CN)₄]⁻ pale blue? Could the “cubic material” found in the LDH ferrocyanides be the same compound we see here, ala nickel?
Comment: Hexacyanoplatinate(IV) was also exposed to 2:1, 3:1 and 4:1 Mg:Al LDH systems, in order to investigate its behavior on intercalation. However, the \([\text{Pt(CN)}_6]^2^-\) anion does not intercalate significantly into 2:1 or 3:1 Mg:Al LDHs, requiring instead a Mg:Al ratio of 4:1 before intercalating in large amounts. We think this is due to the density of positive charges in the layers of 2:1 and 3:1 LDHs; in these cases, \([\text{Pt(CN)}_6]^2^-\) cannot effectively coordinate to positive centers inside the layer, presumably because of the size of the anion. Instead, it adsorbs on the outer surfaces of the material only, and allows carbonate or chloride (the parent LDHs were LDH chlorides so as to avoid possible reactions with the alternative nitrate parents) to intercalate instead. When the Mg:Al ratio approaches 3:1, the charge density is low enough to permit \([\text{Pt(CN)}_6]^2^-\) to intercalate successfully. Figure 23 shows the IR spectrum of the 3:1 \([\text{Pt(CN)}_6]^2^-\) material, however, IR data for the 2:1 and 4:1 systems of this material is currently missing. This phenomenon must be investigated more thoroughly before any publishable data is available.

Comment: I was not satisfied with this explanation until I constructed a very elaborate 3-dimensional model of an LDH system with two intercalated \(\text{O}_n\) anions. Attempts to model the LDH ferrocyanide system using PC Spartan Professional Edition were unsuccessful due to limitations of the program (as well as limitations of our understanding of that program). Better versions of Spartan are available for UNIX platforms, but no attempts have been made to continue modeling the system this way.

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cyanide, and formation of diaminomaleonitrile, other as yet unidentified materials, and, at higher concentrations, pink to purple material that appears to be strongly associated with the LDH."

Comment: This material is the main reason for this paper, and is doubtless the start of a very long research project in this area. Had the otherwise white LDH, when exposed to a clear solution made from pure water and white KCN crystals, not turned a sickeningly vibrant shade of red, there would have been no indication that something was special about this system. The IR spectrum of any given LDH-CN system is identical (or very nearly so) to that of an LDH carbonate. The colored material in question invariably turns a purple-violet color after a short while. I can only recall one time I managed to get a pink/red LDH-CN system successfully centrifuged, washed, and dried without it changing color. It displayed the same characteristics as the purple systems did in the IR.

The colored material itself is strongly bound to the LDH somehow; perhaps it is a branched cyanide polymer with many areas of negative charge. No attempts to remove it from the layer have been followed through to my knowledge; "gently" dissolving the LDH layer by exposing the solution to anion exchange resin yielded a questionable aqueous solution with a very faint purple color. Isolation of any solids from this solution proved impossible at the time due to then unknown problems with the Rotovapor apparatus. This will doubtless be an area of future research, along with further HPLC analysis. As with any interesting polymerization, it will be impossible to identify all of the products; for our purposes, however, we need only search for those which are of prebiotic interest.
Figure 23. Infrared spectrum of 3:1 LDH hexacyanoplatingate (nonoriented).
Layered Double Hydroxides can successfully intercalate many metal-cyanide complexes, however, this intercalation is subject to certain conditions, such as layer charge density, anion charge density, and presence of carbonate in the interlayer. Cobalticyanide is shown to intercalate into Mg:Al LDHs in a manner similar to ferrocyanide, with its 3-fold axis perpendicular to the positive charges of the layer. The anion is shown by IR and XRD data to distort to $D_{3d}$ from its optimal $O_h$ symmetry on intercalation. Hexacyanoruthenate(II) anions were also intercalated into 2:1 and 3:1 Mg:Al LDHs, exhibiting behavior similar to the other metal-cyanide complexes of coordination number 6.

The behavior of square-planar metal-cyanide complexes on intercalation into 2:1 and 3:1 Mg:Al systems was also analyzed by IR and XRD studies, with metal ratios determined by ICP analysis. The anions showed significant amounts of intercalation in all cases, including what we believe to be the first known intercalation of Pd and Pt complexes of any kind into a layered double hydroxide system. XRD studies indicate that the anions in the 2:1 systems are inclined at an angle of approximately 75° relative to the layer, while in the 3:1 systems they are more or less parallel to the layer. Further investigation of the change in the Ni:C ratio on intercalation of square-planar $[\text{Ni(CN)}_4]^{2-}$ complexes is necessary to understand the implied change in coordination number on intercalation of this compound. The analysis should also be expanded to include other, possibly more active square-planar complexes, such as $[\text{Pt(CN)}_4]^{2-}$. Solid-state $^{13}$C-NMR studies may offer some new information on this phenomenon, by allowing comparison of the environments of each –CN group in the interlayer.

Controlled uptake of Pt-CN complexes was shown with the $[\text{Pt(CN)}_4]^{2-}$ and $[\text{Pt(CN)}_6]^{2-}$ anions in the case of Mg:Al LDH systems. Hexacyanoplatinate(IV) anion does not into 2:1 Mg:Al LDH, preferring to adsorb onto the outer surfaces only, while the tetracyanoplatinate(IV) anion intercalates readily. When the Mg:Al ratio is ~3:1, $[\text{Pt(CN)}_6]^{2-}$ shows a small degree on intercalation, as evidenced by the IR spectrum displayed in the Commentary section of Part II of this paper. Greater levels of
intercalation are obtained when the Mg:Al ratio is 4:1. More thorough investigation of this phenomenon would allow a greater insight into the nature of hydrogen bonding and charge density in LDH systems in general. Catalytically important metals (besides Pd and Pt) may also intercalate in this manner, allowing for the possibility of controlled release of catalytic metal complexes into reactions where they are “poisoned”. Further treatment of adsorbed materials could allow for surface activation of these complexes and thus hinderance of one side of the complex to produce a chiral environment.

2:1 Mg:Al layered double hydroxides are shown to catalyze a novel self-addition of free cyanide in solution to give a wide variety of addition products, many of which are as yet unidentified. The most prevalent product in solution is diaminomaleonitrile, the tetramer of cyanide. The self-addition reaction is expected to be in competition with hydrolysis to formamide under the conditions that the experiment was performed. This is evidenced by the equivalent experiment with the 3:1 material, in which self-addition products were not as prevalent as in the 2:1 case. Since cyanide polymerization pathways contain nucleobases as possible products, this catalysis is of interest in the origins of life, and could prove to be a likely candidate for prebiotic synthesis on the early Earth.

In addition to simple cyanide tetramers and oligomers, the reaction also produces a pink-purple colored material that stays intimately associated with the LDH. The color of this material varies in intensity depending on the amount of LDH present, the [CN] in solution, and the amount of carbonate phase present. Future work in this area should include development of isolation and characterization techniques for this material, in an effort to better understand how much of the cyanide is potentially made unavailable to more biologically relevant chemistry. Better separation of the compounds present in solution may afford a greater understanding of this reaction, as well as furnishing more information for kinetic studies. More information about the nature of the colored material could be gained from scanning electron micrographs; this could determine if the material is part of the layer or merely intimately mixed with it.
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31. Available as Supporting Information.


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67. Bocclair, J. W.; Braterman, P. S.; Brister, B. D. To be published.
Glossary

**Accretion** - The buildup of particles into larger particles by gravity; in the case of the early solar system, this consisted of clumps becoming planetesimals, which then attracted more and larger rock bodies towards them to become planets.

**Analyte** - The compound, ion, or radical of interest in a system that is being examined.

**Anion** - a negatively charged ion (e.g. Cl⁻).

**Cation** - a positively charged ion (e.g. Na⁺).

**Chiral** - having a non-superimposable mirror image. A common analogy uses hands: left hands are non-superimposable on their mirror imaged right hands.

**Cyanide** - [CN], see Potassium Cyanide.

**DAMN** - DiAminoMaleoNitrile; the tetramer of cyanide. See also Polymerization.

**Equivalent** - the amount of compound needed to equal the amount needed of another in a synthesis. For example, LDH synthesis uses 3 equivalents of Mg salt, 1 equivalent of the Al and Na salts, and 1 equivalent of NaOH.

**HPLC** - High Pressure Liquid Chromatography; a method for separating components from a common solution. The solution is pumped through a column of material (the stationary phase) which selectively slows compounds of one type while allowing another type to pass through more quickly. Usually the sample is mixed with a standard solution (the mobile phase) to allow greater sensitivity. The pump runs the solution through the column under a very high pressure (2,000 psi), then into a detector. Modern detectors come in a variety of types and can produce spectra, refractive indices, or measurements of some other type.

**Hydrochloric Acid** - HCl; also called muriatic acid. HCl is often used in swimming pools to lower the pH, in the laboratory to clean glassware, and is a key component of stomach fluid.

**ICP** - Inductively Coupled Plasma. This is primarily used to determine ratios of one metal to another in LDH systems. High voltage from a RF (Radio Frequency) generator is passed through a coil of wire around a jet of argon gas. The argon atoms become excited enough to form a plasma, which small amounts of analyte solution can be fed into. Metal ions get excited by the plasma and give off light,
which a detector then measures. The ICP data gives information on the
concentration of each metal element in solution; further calculations give the
desired metal ratios. In order to run an ICP, the analyte must be broken into
dissolved ions (digested) so as not to plug the nozzle of the argon/solution jet.
Various concentrations of different acids (usually nitric or hydrochloric) are used
to digest samples.

**Intercalation**- substitution of one compound for another in the space between two layers
of material.

**LDH**- Layered Double Hydroxide.

**Molarity**- a measure of concentration in solution; Molarity (M) = \#moles of solute per
Liter of solvent.

**Mole**- 6.0221367x10²³ units of anything, usually molecules or atoms.

**Monomer**- The single unit from which a polymer is made, usually a simple compound.

**NIR**- Near InfraRed; the part of the IR spectrum closest to the visible region.

**Nitric Acid**- HNO₃; a common acid used to decompose LDH systems for ICP and to
clean glassware.

**Oxidation-Reduction**- A common class of chemical reaction, in which one molecule
loses electrons to another. *Oxidation* is electron loss; *reduction* is electron gain,
often accompanied by gaining a hydrogen atom as well. Thus, ammonia (NH₃) gets reduced to ammonium [NH₄]⁺ and methane (CH₄) gets oxidized to carbon
dioxide (CO₂). Also known by the acronym REDOX.

**pH**- Formally defined as \(-\log_{10} [H^+]\), this is a measure of the hydrogen ion concentration,
\([H^+]\). The higher the \([H^+]\), the lower the pH; thus, hydrochloric acid has a pH of
1, while sodium hydroxide (NaOH) has a pH of about 10.

**Polymerization**- Bonding of two monomers together, with subsequent additions of more
monomer, until a chain or complex of \(n\) monomers is formed.

**Potassium Cyanide**- KCN; a deadly inhibitor of cellular respiration and favored poison
of the Russian Mafia. All known antidotes (e.g. potassium nitrite, KNO) are
themselves poisonous. Cyanide anion (CN⁻) readily reacts in solution to give
DAMN and other products.
**Reducing**- a term describing a substance which normally gives electrons to other compounds. See also *oxidation-reduction*.

**Reflux**- boiling a solution in such a manner as to allow vaporous materials to condense and fall back into solution. A solution is said to be refluxing whenever solution boils in this manner. Normally, a jacketed water condenser is used.

**Subduction**- Forcing of denser crust material underneath lighter crust material, causing the crust to melt and mix with new rock from the mantle.

**Thermogravimetric**- A method of analysis that involves repeated heating and weighing of a product to determine what other stable compounds (e.g. water, CO₂) are trapped in the product.

**Titration**- Very slow (usually drop-by-drop) addition of one solution to another; usually used for quantitative measurements.

**UHP**- Ultra High Purity, 99.9998% or higher in purity.

**XRD**- X-Ray Diffraction. X-rays of certain wavelengths can be scattered by atoms, giving distinctive trace patterns that give information about the crystal structure of the compounds studied. One of the most common sources for X-ray radiation comes from bombarding metal atoms with high voltage electrons, knocking electrons from the atoms’ innermost energy levels (shells). As electrons from higher energy shells relax into the holes formed, X-rays are emitted at various wavelengths. The electron transitions (shifts from one energy level to another) are designated K, L, M, N, etc. by the shell the electrons fall into. The subscripts α, β, and γ show whether the transitions start one, two, or three shells away before reaching their final state. For example, Mo Kβ X-rays would come from a molybdenum atom, where the electron relaxed into the K shell from two shells above (the M shell).