Layered structures are characterized by strong (and typically covalent) bonding between atoms in two dimensions and weaker bonding in the third. A broad range of compounds including metal halides, oxides, sulfides, selenides, borides, nitrides, carbides, and allotropes of some pure elements (B, C, P, As) exist in layered forms. Structurally, the simplest of these structures (for example binary metal halides and sulfides) can be described as having some fraction of the octahedral and/or tetrahedral sites are filled in the fcc and hcp lattices. For example, the CdCl₂ structure is formed by filling all the octahedral sites in alternate layers of the fcc lattice, and the CdI₂ structure is the relative of this structure in the hcp lattice.

In the CdCl₂ structure, the stacking sequence of anion layers is ABCABC...
In the CdI₂ structure, the anion stacking sequence is ABAB..., and all the cations are eclipsed along the stacking axis.

Comparison of the CdCl₂ (left) and CdI₂ (right) crystal structures

These are examples of 6-3 structures, because the cations are coordinated by an octahedron of six anions, and the anions are coordinated by three cations to make a trigonal pyramid (like NH₃). Another way to describe these structures is to say that the MX₆ octahedra each share six edges in the MX₂ sheets.

Polyhedral drawing of one layer of the CdCl₂ or CdI₂ structure showing edge-sharing MX₆ octahedra

Because these structures place the packing atoms (the anions) in direct van der Waals contact, they are most stable for relatively covalent compounds. Otherwise, the electrostatic repulsion between contacting anions would destabilize the structure energetically. More ionic MX₂ compounds tend to adopt the fluorite (CaF₂) or rutile (TiO₂) structures, which are not layered.
Despite the fact that these two structure types are the same at the level of nearest and next-nearest neighbor ions, the CdI$_2$ structure is much more common than the CdCl$_2$ structure.

**CdCl$_2$ structure:**

\[
\text{MCl}_2 (\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd})
\]

\[
\text{NiBr}_2, \text{NiI}_2, \text{ZnBr}_2, \text{ZnI}_2
\]

**CdI$_2$ structure:**

\[
\text{MCl}_2 (\text{M} = \text{Ti}, \text{V})
\]

\[
\text{MBr}_2 (\text{M} = \text{Mg}, \text{Fe}, \text{Co}, \text{Cd})
\]

\[
\text{MI}_2 (\text{M} = \text{Mg}, \text{Ca}, \text{Ti}, \text{V}, \text{Mn}, \text{Fe}, \text{Co}, \text{Cd}, \text{Ge}, \text{Pb}, \text{Th})
\]

\[
\text{M(OH)}_2 (\text{M} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cd})
\]

\[
\text{MS}_2 (\text{M} = \text{Ti}, \text{Zr}, \text{Sn}, \text{Ta}, \text{Pt})
\]

\[
\text{MSe}_2 (\text{M} = \text{Ti}, \text{Zr}, \text{Sn}, \text{V}, \text{Pt})
\]

\[
\text{MTe}_2 (\text{M} = \text{Ti}, \text{Co}, \text{Ni}, \text{Rh}, \text{Pd}, \text{Pt})
\]

Physically, layered compounds are **soft** and **slippery**, because the layer planes slide past each other easily. For example, graphite, MoS$_2$, and talc (a silicate) are layered compounds that are used widely as **lubricants** and lubricant additives.

An important reaction of layered compounds is **intercalation**. In intercalation reactions, guest molecules and ions enter the galleries that separate the sheets, usually with expansion of the lattice along the stacking axis. This reaction is typically reversible if it does not perturb the bonding within the sheets. Often the **driving force for intercalation** is a **redox reaction**, i.e., electron transfer between the host and guest. For example, lithium metal reacts with TiS$_2$, MoS$_2$, and graphite to produce LiTiS$_2$, Li$_x$MoS$_2$ ($x < 1$), and LiC$_6$. In these compounds, lithium is ionized to Li$^+$ and the sheets are negatively charged. Oxidizing agents such as Br$_2$, FeCl$_3$, and AsF$_5$ also react with graphite. In the resulting intercalation compounds, the sheets are positively charged and the intercalated species are anionic.

Intercalation reactions are especially important for electrochemical energy storage in **secondary batteries**, such as **lithium ion** batteries, **nickel-metal hydride** batteries, and **nickel-cadmium** batteries. The reversible nature of the intercalation reaction allows the electrodes to be charged and discharged up to several thousand times without losing their mechanical integrity. In lithium ion batteries, the negative electrode material is typically graphite, which is intercalated by lithium to make LiC$_6$. Several different oxides and phosphates containing redox active transition metal ions (Mn, Fe, Co, Ni) are used as the positive electrode materials.
Oxidative or reductive intercalation involves the placement of anions or cations between sheets.

Lithium ion batteries based on CoO$_2$ were first described in 1980[1] by John B. Goodenough's research group at Oxford. In batteries based on CoO$_2$, which has the CdI$_2$ structure, the positive electrode half-reaction is:

\[ \text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_{2} + x\text{Li}^+ + xe^{-} \]

The negative electrode half reaction is:

\[ x\text{Li}^+ + xe^{-} + x\text{C}_6 \rightleftharpoons x\text{LiC}_6 \]

The battery is fully charged when the positive electrode is in the CoO$_2$ form and the negative electrode is in the LiC$_6$ form. Discharge involves the motion of Li$^+$ ions through the electrolyte, forming Li$_x$CoO$_2$ and graphite at the two electrodes.

Blue plaque erected by the Royal Society of Chemistry commemorating the development of cathode materials for the lithium-ion battery
The lithium ion battery is a "rocking chair" battery, so named because charging and discharging involve moving Li$^+$ ions from one side to the other. CoO$_2$ is one example of a positive electrode material that has been used in lithium ion batteries. It has a high energy density, but batteries based on CoO$_2$ have poor thermal stability. Safer materials include lithium iron phosphate (LiFePO$_4$), and LiMO$_2$ (M = a mixture of Co, Mn, and Ni). These batteries are used widely in laptop computers, portable electronics, cellular telephones, cordless tools, and electric and hybrid vehicles.

A similar intercalation reaction occurs in nickel-cadmium batteries and nickel-metal hydride batteries, except in this case the reaction involves the movement of protons in and out of the Ni(OH)$_2$ lattice, which has the CdI$_2$ structure:
\[
\text{NiO(OH) + H}_2\text{O + e}^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^-\]

There are many layered compounds that cannot be intercalated by redox reactions, typically because some other stable product is formed. For example, the reaction of layered CdI\(_2\) with Li produces LiI (NaCl structure) and Cd metal.