Organic-inorganic hybrids
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Chapter 1

Introduction to Organic-Inorganic Hybrids

1.1 Hybrids? The Best of Both Worlds

According to the Oxford English dictionary\(^1\) a hybrid is a system that is “Derived from heterogeneous or incongruous sources; having a mixed character; composed of two diverse elements; mongrel.” In practice, the term hybrid is used to denote (biological) inbreed, cars, laptops\(^2\) and (of course in the Netherlands) bikes.\(^3\) Also within physics and chemistry “hybrid” is used in various contexts. It can refer to theoretical models\(^4\) as well as macroscopic multilayer devices\(^5\) and composites. In this thesis we use the term “organic-inorganic hybrids” for crystalline materials that combine inorganic and organic constituents on a molecular scale.

Organic materials consist mainly of the elements carbon and hydrogen, with the possibility of additional nitrogen, oxygen and sulfur. Those elements are denoted with the black circle in figure 1.1. They are the main ingredient of living species, from cellulose to hormones and fats! Organic materials also have many industrial applications, such as plastics and dyes. The raw organic materials that are used for these applications are (indirectly) deduced from natural organic sources such as petroleum. The organic materials are mostly used in applications that require easy processing, low costs and flexibility. Those three unique parameters triggered research efforts to fabricate organic materials that are suitable for electronics. In the last years the first organic electronic applications came on the market in (flexible) displays\(^6\) and organic light emitting diodes (OLED).\(^7\)

Inorganic literally means not-organic. The inorganic elements cover most of the periodic table, see figure 1.1. Inorganic materials often need high-tech and high-power equipment to be processed. However their robust and high-performance electric and magnetic properties are unequalled and therefore the inorganic materials are extensively used in conventional electronics.
In this thesis we present the synthesis and characterization of organic-inorganic hybrids, in which it is tried to combine the best of both the organic and the inorganic materials. We explore the possibilities of organic-inorganic hybrids for electronic applications and focus on the design of materials that combine solubility with ferromagnetism and semiconductivity. Those materials could be of interest for applications in cheap and printable single-use electronics that require both data storage and data processing. Moreover, this combination of unique parameters is rarely observed in conventional materials and is therefore, also from a fundamental point of view, an interesting place to start the exploration of the field of organic-inorganic hybrids.
1.2 Classification of Organic-Inorganic Hybrids

In this thesis we discuss crystalline hybrids that combine inorganic and organic materials on a molecular scale. But even this subclass of organic-inorganic materials consists of a tremendous number of materials. Before we get lost in the complexity and diversity, we will classify the hybrids on the basis of the model of Cheetham et al. They proposed a classification system based on connectivity of the inorganic and organic components inside the crystalline hybrid material. Only covalent and ionic bonds are counted in this system and all others, such as hydrogen bonds and van de Waals bonds, are ignored. The classification system is tabulated in figure 1.2. The $I^n$ denotes the dimensionality of the inorganic connectivity. Thus when a material belongs to the $I^2$ group, the inorganic component has an infinite 2 dimensional connectivity and will form sheet-like arrays. The $O^n$ denotes the metal-organic-metal connectivity. For example, the $O^3$ group consists of materials, in which the metal is bound to another metal via the organic molecule in all three dimensions. The classes of $I^0O^0$, $I^1O^1$ and $I^2O^2$ are schematically represented in figure 1.3. The square denotes the inorganic moiety and the circle the organic component. The black lines indicate an ionic or covalent interaction.

<table>
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<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>0</td>
<td>$I^0O^0$ Molecular Complex</td>
<td>$I^1O^0$ Inorganic Network Hybrid</td>
<td>$I^2O^0$ Inorganic Network Hybrid</td>
<td>$I^3O^0$ Inorganic Network Hybrid</td>
</tr>
<tr>
<td>1</td>
<td>$I^0O^1$ Coordination Polymer</td>
<td>$I^1O^1$ Mixed Layers</td>
<td>$I^2O^1$ Mixed Framework</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>$I^0O^2$ Coordination Polymer</td>
<td>$I^1O^2$ Mixed Framework</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>$I^0O^3$ Coordination Polymer</td>
<td>—</td>
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**Figure 1.2:** The Classification of the crystalline organic-inorganic materials as proposed by Cheetham et al. The materials are classified on the basis of the dimension of the inorganic connectivity $I^n$ and the dimension of the metal-organic-metal connectivity $O^n$. The n denotes the dimensionality of the connections. This table is adapted from Cheetham et al.
Chapter 1

The largest class is the $\text{I}^0\text{O}^0$ category, it consists of all organic-inorganic molecular complexes. The class includes all metal ions that are coordinated by organic molecules such as hemoglobin and ferrocene. In general there is little connectivity between the metal centers, neither directly nor via the inorganic and organic ligands, and therefore the long range magnetic order can not be maintained inside these hybrids. Nevertheless, electronically interesting properties have been obtained in this class of materials, such as the superconductivity in charge-transfer salts; The $\text{I}^0\text{O}^0$ hybrids based on the organic components BEDT$^9$ or Bucky-balls have transition temperatures as high as 40 K ($\text{Cs}_3\text{C}_{60}$)$^{10}$ The latter is also often regarded as a doped organic material instead of an organic-inorganic hybrid, as the isolated Cs ions only function as charge compensation.

The $\text{I}^0\text{O}^0$ (n≥1) subclass is often referred to as coordination polymers. These are called polymers as they consist of endless [metal-organic-metal-organic] arrays in at least one direction. Unlike conventional polymers, these coordination polymers are not disordered but they form crystalline materials. Another difference with conventional polymers is the connectivity: traditional polymers are mostly 1-dimensional while the coordination polymers can be 1, 2 and 3 dimensional. Depending on the size of the organic component the inorganic properties, such as magnetic order, can be reflected in the hybrid material.

![Schematic representation of three examples of organic-inorganic hybrids. The squares and the circles denote the inorganic and organic components respectively. The materials are classified in accordance with the model of Cheetham et al.](image)

Figure 1.3: Schematic representation of three examples of organic-inorganic hybrids. The squares and the circles denote the inorganic and organic components respectively. The materials are classified in accordance with the model of Cheetham et al. These pictures assume no connection in the direction perpendicular to the depicted plane.
Especially for very small organic “spacers” such as the C-N in Prussian blue\textsuperscript{11} $\text{M1M2(CN)}_6$ (M1 and M2 are transition metals), there is communication between the magnetic ions and long range magnetic order is obtained with ordering temperatures as high as 70 K.\textsuperscript{12} Throughout the literature, the Prussian blue compounds are regarded as hybrids that belong to the $\text{I^0O}^3$ class. However, it is disputable if such a small organic spacer justifies the term “organic molecule”. After all, inorganic metal oxides are inorganic atoms connected with the organic atom: oxygen, but they are definitely not part of the organic-inorganic hybrids family. In this thesis we restrict organic molecules to moieties with 3 or more atoms, and thus we do not consider the Prussian blue analogues as hybrids. Hybrids of the $\text{I^0O}^0$ subclass with large organic molecules form porous structures in which the magnetic interactions are small. In this context, the coordination polymers are often referred to as Metal Organic Frameworks (MOFs). These porous coordination polymers are currently being investigated for their interesting gas separation and hydrogen storage properties.\textsuperscript{13} In the search for a soluble ferromagnetic semiconductor, we focus on the $\text{I^{1-3}O}^0$ materials. In this class of organic-inorganic materials there is a direct connection between the inorganic moieties that allows for strong magnetic interactions. Therefore, those materials are the best candidates for showing long range magnetic order with high ordering temperatures.

\section*{1.3 Magnetic Organic-Inorganic Hybrids [$\text{I^{1-3}O}^0$]}

In this section we will give a short review on the magnetic properties in the $\text{I^0O}^0$ organic-inorganic hybrids ($n=1$, 2, 3). Their strong magnetic interaction allows magnetic ordering temperatures that are accessible for electronic applications. In the inorganic-network-hybrids, $\text{I^{1-3}O}^0$, the magnetic ions are in close proximity of each other. Strong magnetic interactions are facilitated by direct and superexchange paths. In this review we will we also include the carboxylate, sulphonate, nitro and phosphonate bridged inorganic networks, because of the small distance between the metal centers, although they are, strictly spoken, coordination polymers. This overview is based on the reviews given by Cheetham et al.\textsuperscript{8,14} and Rabu et al.\textsuperscript{15}
1.3.1 Intercalates

Intercalates consist of sheet-like inorganic guest materials. Under certain conditions, these layers move apart and organics can be inserted between the layers, as is schematically shown in figure 1.4. Probably the most famous intercalation compounds are clays (2-D silicon-aluminate frameworks) and graphite (2-D carbon framework). Also magnetic intercalation hosts are known that are based on phosphorous trichalcochenides (MPS\(_3\)) (with M=divalent transition metal). In these materials, the host consists of divalent metal ions that are interconnected via \((\text{P}_2\text{S}_6)^4\) bridging ligands. It can be intercalated by any positively charged cation, this charge is compensated by the introduction of metal vacancies in the inorganic host layers. The host material based on Mn\(^{2+}\) is antiferromagnetic below 78 K. An external magnetic field perpendicular to the inorganic sheets induces a spin flop at a 40 Oe (= 4*10\(^{-3}\) Tesla). In its intercalation compounds weak ferromagnetism is observed with ordering temperatures ranging between 15 and 45 K. The lowering of the ordering is due to the introduction of metal vacancies that dilute the spin lattice. The FePS\(_3\) orders at 123 K, but is much harder to intercalate than the Mn-based material. These intercalates show ferrimagnetic ordering temperatures between 70 and 90 K.

Also the transition-metal dichalogenides have the possibility to intercalate organic molecules. The inorganic host materials have been extensively studied. They are semiconducting, semimetallic and sometimes superconducting. Magnetic ordering temperatures as high as 140 K are reported.

![Figure 1.4: A schematic representation of the intercalation process. The black squares denote the inorganic and the circles the organic component. The intercalation compounds consist of an inorganic sheet-like host material (left). The added organic molecules penetrate between the inorganic sheets to form the organic-inorganic hybrid (right).](image-url)
The dichalcogenides can be intercalated with various organics, such as alkyldiamines. The intercalation processes and electric properties of the organic-inorganic intercalates are well documented. Although the organic-inorganic intercalates are expected to show high magnetic ordering temperatures, few magnetic studies have been performed.

1.3.2 Oxygen Bridged

In the oxygen-bridged inorganic network hybrids the magnetic divalent transition-metals are interconnected by phosphonate, carboxylate, nitro or sulphonate groups, see figure 1.5. In most cases the metal ions are surrounded by an octahedron of oxygen atoms. Each of those oxygen atoms is coupled to another oxygen atom that is part of a different octahedron via an N, S, C or P atom. This intermediate N, S, C or P atom is connected to an R group that consists of an organic moiety ranging from an individual hydrogen atom to larger organic molecules, such as alkyl chains or benzene rings. In this way, a wide variety of inorganic network hybrids can be formed, mostly with 2-dimensional inorganic arrays.

![Figure 1.5: The various bridging groups of the organic ligands used in the oxygen bridged organic-inorganic hybrids. The sulphonate and phosphonate groups can bridge 3 metal centers (M). The nitro and carboxylate bridging ligands can bridge 2 metal centers. The R denotes a variable organic molecule.](image-url)
In some cases, hydroxyl-ions or water molecules are present in the material to bridge the metals in the directions that are sterically out of range for the large bridging molecules.

In the oxygen-bridged hybrids, long range magnetic ordering occurs with transition temperatures up to 65 K.\textsuperscript{8} The magnetic exchange is based on superexchange interactions that are mediated by the bridging atoms. Therefore, the type of magnetic order depends on the metal ions involved and on the Metal-Oxygen-Metal angles. The highest ordering temperatures are observed for the hybrids based on carboxylates such as \(\text{Co}_5\text{(OH)}_8\text{(chdc)}\) (chdc=trans-1,4-cyclohexanecarboxylate), which is ferrimagnetic\textsuperscript{27} below 60 K and the \(\text{AFe}_2(\text{ox})_3\) (\(\text{A}=\text{N(propane)}_4^+\) and \(\text{ox}=\text{oxalate}\)) that orders ferrimagnetically below 48 K (due to the coexistence of both \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\)).\textsuperscript{15}

### 1.3.3 Halide Bridged

The halide-bridged organic-inorganic hybrids consist of inorganic arrays in which divalent metal ions are connected via a single halogen atom. These inorganic components can form a wide variety of structures with varying dimensionality. However, the most common structure is the perovskite-like structure.\textsuperscript{28}

![Diagram](image)

**Figure 1.6:** Side view of an \(O^\text{\textsuperscript{2+}}\) halogen-bridged inorganic network hybrid. The corner sharing \(\text{MX}_6\) octahedra form 2-dimensional perovskite-like layers that are negatively charged. The metal ions are denoted by the black dots and the halogens by the grey dots. The charge of the inorganic layers is compensated by the positively charged ammonium ion (denoted by the triangle) connected to the organic molecule (denoted by the oval).
Here, the metal ions are octahedrally coordinated by the halogen atoms and these octahedra share their corners to form a perovskite-like sheet. These perovskite layers have a net charge of -2 per formula unit, which is compensated by positively charged RNH$_3^+$ ions that are present between the inorganic layers. The R group can vary from a hydrogen atom to larger organic molecules such as phenylethyl or alkane chains up to n=14 (longer chains do hardly occur due to their poor solubility). Depending on the size of R, also 3 dimensional perovskite structures can be formed (I$^3$O$^0$).

Most recent research is performed on the non-magnetic halide bridged organic-inorganic hybrids based on lead and tin. In the previous century, however, hybrids based on magnetic divalent transition-metals were thoroughly studied. A good review of this early work is given by Miedema en de Jongh. Such systems can show long range magnetic order with transition temperatures up to 100 K. The magnetic exchange is based on superexchange. The type of magnetic order ranges from ferromagnetic to antiferromagnetic, depending on the transition metals that are used. The highest ordering temperatures are observed for the Fe-bases hybrid. Moreover, the ordering temperatures do also depend on the organic component: They are highest when short diammonium R-groups are used. For example NH$_3$C$_2$H$_4$NH$_3$CuBr$_4$ shows long range ferromagnetic ordering below T$_c = 72$ K and the (NH$_3$C$_2$H$_5$)$_2$CuBr$_4$ below T$_c = 11$ K.

1.4 Motivation and Research Aim

The aim of this thesis is to design organic-inorganic hybrids that combine the best of both the organic and inorganic characteristics. We search for materials that are interesting for electronic applications and combine the unique parameters of solubility with ferromagnetism and semiconductivity. We will focus our research on the halide-bridged hybrids with the general composition (YNH$_3$)$_n$MX$_{3n+1}$. These inorganic network hybrids belong to the I$^{1-3}$O$^0$ class and have long range inorganic connectivity that results in strong magnetic interactions. Magnetic ordering temperatures as high as 100 K have been reported for these halide based hybrids. The non-magnetic members of this class of materials are reported to show excellent semiconducting properties. Kagan et al. showed that spin-coated field effect transistors of the tin based hybrid can show electric mobilities as high as 1
cm²/Vs. This is one of the highest values that is reported for solution processed semiconductor devices. A wide variety of different organic and inorganic starting compounds was successfully incorporated in this type of hybrids. Therefore, it is expected that enough tools are available to further optimize the properties of these hybrids.

In this thesis, we present a systematic study on the relations between the composition, the crystal structure and the electric and magnetic properties of a series of transition-metal-based organic-inorganic hybrids, with the general formula $\text{MCl}_{3+x}(\text{YNH}_3)_{1+x}$ ($\text{M}=\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ or $\text{Cu}^{2+}$ and $\text{Y}$ is an organic molecule). We investigate if this class of hybrids can combine ferromagnetism and conductivity and point out which parameters play a role in optimizing the magnetic and electronic characteristics.

1.5 Outline of this Thesis

The next chapter, Chapter 2, gives a short overview of the basic chemistry and physics that is required to understand the contents of the thesis. Chapter 2 will give readers with a different scientific background the opportunity to understand the main findings of this thesis.

Chapter 3 will discuss the synthesis and structure of $\text{MCl}_{3+x}(\text{YNH}_3)_{1+x}$ ($\text{M}=\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ or $\text{Cu}^{2+}$ and $\text{Y}$ is an organic molecule). In this chapter we discuss the variety of structures that occur for these materials and the possible correlations between the chemical composition and the final hybrid structure.

Chapter 4 discusses the magnetic properties of the halide bridged hybrids. The crystal structure and the dimensionality of the inorganic backbone dictate the type of magnetic ordering in the hybrids. There is debate on which factors determine the maximum ordering temperature. An overview of the various scenarios is also given in this chapter.

The electric properties of the hybrids are discussed in chapter 5. Their band gaps are estimated by temperature dependent I-V measurements. Besides, the use of chemical electron doping to increase the number of carriers is discussed.

In chapter 6, the possibilities for multiferroicity in the hybrids are explored on the basis of the examination of a polar phase transition in the ferromagnetic Cu-hybrid.
References


Introduction to Organic-Inorganic Hybrids

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