Chapter 6. Tuning the intra-chain magnetic exchange constant in S=1 quasi one-dimensional NiCl-based hybrids

6.1 Introduction

The family of quasi one-dimensional Ni-based organic-inorganic hybrids, with general formula NiCl₃(XNH₃)₂ can be synthesized with a large variety of ligands X including alkyls C₂H₅, C₃H₇, phenyl C₆H₅, and benzyls C₆H₅CH₂ and C₆H₅C₂H₄. This family of materials represents the I¹O² class of hybrids in the Cheetham classification of hybrids¹. In these hybrids the magnetic dimensionality is dictated by the inorganic backbone, formed by chains of face-sharing octahedra NiCl₆, coordinated by the amine and the organic molecules. This family of hybrids represents S=1 Heisenberg antiferromagnetic spin chains, and attracts significant interest as model magnetic systems², Haldane gap compounds³,⁴ and for low-dimensional thermal transport phenomena⁵,⁶.

I will show that the magnetic properties of the inorganic block can be finely tuned by using different organic moieties. Different organic moieties cause structural modifications, resulting in changes of the intra-chain magnetic interactions. The in-chain nearest neighbor exchange constants J can be varied considerably, even though the Ni-Ni distances and Ni-Cl-Ni angles in the chain are very similar. This chapter will discuss the influence of the organic moieties on the variations of the magnetic properties in these Ni-based hybrids.
6.1.1 Ni-based one-dimensional magnetic systems

As discussed in Chapter 1, the magnetic moments in our hybrids originate from unfilled electron shells of the transition metal ions. In the crystal the magnetic moments interact with each other via superexchange interactions. This interaction depends non-exponentially on the distance between the magnetic ions. In case of low dimensional systems, these superexchange interactions are much stronger along particular directions\(^2\)\(^,\)\(^7\). In other words, the exchange constant \(J\) is much different for different directions. In this situation long-range order is suppressed, and only short-range interactions should be considered. The NiCl\(_3\)-type hybrids form (quasi) one-dimensional magnetic systems.

Considerable progress in the understanding of the physics of low-dimensional spin systems was achieved by studying a variety of quasi-one dimensional systems. The well-known example \([N(CH\textsubscript{3})\textsubscript{4}]MnCl\textsubscript{3}\), TMMC\(^8\), represents a \(S=5/2\) antiferromagnetic Heisenberg chain compound with an intrachain exchange constant \(J/K_\text{B}=-6.7\text{K}\). TMMC is one of a large series of compounds with general formula \(\text{ABX}_3\). Other systems from this family are \(\text{CsCuCl}_3\)\(^9\), \(\text{CsNiF}_3\)\(^10\), quasi one-dimensional ferromagnets \([(\text{CH}\textsubscript{3})\textsubscript{4}\text{N}]\text{NiCl}_3\) (TMNC), \([(\text{CH}\textsubscript{3})\textsubscript{3}\text{NH}]\text{NiCl}_3\cdot2\text{H}_2\text{O}\) (TMAN), and \([\text{C}_9\text{H}_7\text{NH}]\text{NiCl}_3\cdot3/2\text{H}_2\text{O}\)\(^11\).

Interestingly, compounds based on MnCl\(_3\) inorganic parts with different organic cations were previously synthesized: \(\text{CsMnCl}_3\)\(^12\), \((\text{CH}_\text{3}\text{NH}_3)\text{MnCl}_3\cdot2\text{H}_2\text{O}\), \([(\text{CH}_\text{3})_2\text{NH}_2]\text{MnCl}_3\cdot2\text{H}_2\text{O}\)\(^13\). These systems have same inorganic part- cis\([\text{MnCl}_4(\text{OH}_2)_2]\) octahedra, which defines the overall magnetic character. The intra-chain magnetic exchange constants remain approximately the same, even though small distortions are present.

In this chapter a series of NiCl\(_3\)-based compounds is presented in which the intrachain exchange constant \(J\) can be varied by choice of the ligands while keeping the intra- and inter-chain architecture the same.
6.1.2 Synthesis and structure of NiCl-based organic-inorganic hybrids

Several compounds with general formula NiCl$_3$(X)$_2$ were synthesized to investigate the structural variations caused by different organic ligands, where X=C$_2$H$_5$ NH$_3$ (ethylamine EA), C$_3$H$_7$ NH$_3$ (propylamine PA), C$_6$H$_5$ NH$_3$ (aniline AN), C$_6$H$_5$CH$_2$ NH$_3$ (phenylmethylamine PMA) and C$_6$H$_5$C$_2$H$_4$ NH$_3$ (phenylethylamine PEA)). Synthesis procedure and structure determination of these compounds were studied together with T. Poortman, R. Versteeg, S. Blok and P. Noorlailey within their undergraduate projects. The NiCl$_2$ salt was kept at 125°C to evaporate H$_2$O inclusions. The organic salts were purchased from Sigma-Aldrich. The NiCl$_2$ salt and XNH$_3$Cl were mixed in stoichiometric ratio and solved in H$_2$O-free ethanol. After full dissolution of the precursors, the container was covered with an aluminum foil and kept at 60°C until full evaporation of the solvent. The best quality single crystals were chosen using an optical microscope. In order to determine the crystal structure of the hybrids, single crystal X-ray diffraction measurements were performed on a Bruker-Apex D8 diffractometer. Refinements were made by G. Blake and A. Meetsma. Figure 6.1 displays the refined structures of different Ni-hybrids at 100K.

![Figure 6.1](image)

Figure 6.1. Crystal structures of several organic-inorganic hybrids NiCl$_3$(X)$_2$ at 100K, where X= (a)EA, (b)PA, (c)AN, (d)PMA, and (e)PEA.
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<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Monoclinic angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl$_3$(EA)$_2$</td>
<td>Pnma</td>
<td>5.9157(9)</td>
<td>6.8914(10)</td>
<td>16.918(3)</td>
<td>-</td>
</tr>
<tr>
<td>NiCl$_3$(PA)$_2$</td>
<td>Pnma</td>
<td>5.9831(2)</td>
<td>6.9276(3)</td>
<td>18.5320(7)</td>
<td>-</td>
</tr>
<tr>
<td>NiCl$_3$(AN)$_2$</td>
<td>Pbcn</td>
<td>6.8774(2)</td>
<td>20.9592(8)</td>
<td>5.8925(2)</td>
<td>-</td>
</tr>
<tr>
<td>NiCl$_3$(PMA)$_2$</td>
<td>P12$_1$1</td>
<td>6.9420(6)</td>
<td>6.0076(5)</td>
<td>11.6070(11)</td>
<td>101.5$^\circ$</td>
</tr>
<tr>
<td>NiCl$_3$(PEA)$_2$</td>
<td>P2$_12_12_1$</td>
<td>5.8900(2)</td>
<td>6.8797(3)</td>
<td>25.585(1)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.1. Lattice parameters for the Ni-based organic-inorganic hybrids, determined by single crystal X-ray diffraction at 100K in the crystallographically preferred setting.

All Ni-based hybrids belong structurally to the same class with the same Ni coordination and a similar organic-inorganic arrangement. The inorganic backbone of the hybrid is formed by chains of NiCl$_6$ face sharing octahedra. The chains form layers connected by the NH$_3$ tails of the organic ligands. The chain containing layers are in turn separated by the organic ligands. The organic-inorganic connectivity is defined by the hydrogen Cl-H bonding via ammonium groups (NH$_3$).

Table 6.1 displays the lattice parameters of the refined structures of the Ni-hybrids. The hybrids adopt mostly orthorhombic space groups at 100K, except NiCl$_3$(PMA)$_2$, which crystallizes in the monoclinic spacegroup P12$_1$1. The Ni$^{2+}$ atoms have an octahedral Cl-coordination and form chains by face sharing the octahedra. The intra-chain Ni-Ni distance varies from 2.93 to 2.95 Å and the Ni-Cl-Ni bond angles from 75$^\circ$ to 77$^\circ$. The in-plane inter-chain distance is determined by the ammonium tail, which bridges two chains, and ranges from 6.87 to 6.94 Å. The CIF-files of the refinement are presented in the Supplementary Information. Thus, we obtain small structural variations in the inorganic backbone by using different organic moieties.
6.2 Structural behavior of NiCl-based hybrids

Obviously, the length of the organic ligands determines the distance between the chain-bearing layers. This dependence, shown in Figure 6.2a, is approximately linear. Figure 6.2 also displays a more subtle relation of the Ni-Ni distances. In the following, we will focus on how the Ni-Ni intra-chain distance depends on the various organic moieties. This distance is the most important parameter as it defines the magnetic exchange interaction in the system. Due to the different size and geometrical position of the organic moieties in the structure, the Ni-Ni distance along the chain varies from sample to sample. The distortion of the NiCl₆ octahedra follows these changes due to organic-to-inorganic connectivity via H-Cl bonding.

Remarkably, the inter-chain distance increases with increasing intra-chain Ni-Ni distance, as shown in Figure 6.2b. This contrasts with the usual Poisson-type relations between lattice parameter variations. While the inorganic block can be described as a 1-dimensional chain compound, the organic block can for the ring-compounds be described as a herringbone structure. This structure type is often observed for conjugated molecules. It is intermediate to the orthogonal quadrupolar ordering of small conjugated molecules such as naphthalene, and the planar pi-pi-ordering of large planar molecules, such as violanthrene.

Figure 6.2. (a) Dependence of the length of the ligand on the distance between the layers and (b) Ni-Ni interchain distance versus the Ni-Ni intrachain distance.
The packing of the herringbone structures is determined by the interactions of the molecular orbitals near the HOMO and LUMO levels\textsuperscript{14}. The herringbone structure is governed by the angle between the normal vectors of the two planar molecules in the unit cell. For the acenes this angle is roughly 52°. Here the angle is slightly different: 50.9° for AN, 43.6° for PEA, and 47.9° for PMA. There seems no apparent relation between this angle and the Ni-Ni intra- or inter-chain distance. In the present Ni-hybrids the organic and inorganic blocks need to be commensurate along the chain direction. This determines the smallest unit cell parameter, which equals the repeat distance of the organic block and is twice the intra-chain Ni-Ni distance. The bridging of adjacent chains by the amine group determines the middle lattice parameter, linearly related to the intra-chain distance.

### 6.3 Magnetic behavior of NiCl-based hybrids

Single crystal samples of the hybrids were measured using a SQUID magnetometer to reveal their magnetic behavior. High quality needle-like crystals were selected, oriented and fixed with cotton in a gelatin capsule and mounted in a plastic straw. Magnetization versus temperature measurements were performed in a MPMS XL Quantum Design.
magnetometer. Part of the magnetic measurements was performed with P. Noorlaily and T. Poortman.

Figure 6.2a shows the temperature dependence of the magnetization and the inverse magnetization of the Ni-based hybrid crystals. The measurements were performed with the applied magnetic field $H_{\text{ext}} = 0.01\,\text{T}$ parallel to the Ni-chain. To correct for the diamagnetic contributions from the sample holder a temperature independent value of 0.00749 emu/mole was added.

In general, Ni-based chain systems follow the magnetic behavior described by theory of Bonner-Fisher\textsuperscript{15}. We clearly observe broad maxima in the magnetic susceptibility between 10 and 45K. This represents the typical behavior of a 1D magnetic spin chain (Fig. 6.2a). The magnetic susceptibility in the high temperature regime can be fitted

**Figure 6.3.** Magnetic susceptibility versus temperature $\chi(T)$ and $1/\chi(T)$ for different NiCl$_3$(XNH$_3$)$_2$ hybrid compounds, measured at 0.01T field (a). The anomaly at around 47 K is ascribed to a small amount of oxygen inclusions.
for each compound with Curie-Weiss behavior (see inset Fig. 6.2a), in order to determine the effective magnetic moment $p_{\text{eff}}$ and the Weiss interaction temperature $\theta_{\text{CW}}$. The Curie-Weiss law explains the relation between magnetic susceptibilities and the absolute temperature which is valid for ferromagnets, antiferromagnets and paramagnets. The Curie-Weiss law is given by Equation 6.1.

\[
\chi = \chi_0 + \frac{C}{T + \theta_{\text{CW}}} \quad 6.1
\]

Where $C$ is the Curie constant, $\theta_{\text{CW}}$ is the Weiss Temperature, $T$ is the temperature and $\chi_0$ represents the temperature independent contributions. The Curie constant is related to another magnetic property the effective magnetic moment ($p_{\text{eff}}$). This relation is given in Equation 6.2.

\[
C = \frac{Np_{\text{eff}}^2\mu_B^2}{3k_B} \quad 6.2
\]

Where $N$ is the number of magnetic ions, and $\mu_B$ is the Bohr magneton. Using these equations we can calculate the magnetic parameters of antiferromagnetic spin chains, shown in Table 6.2. The negative Curie-Weiss temperature indicates that antiferromagnetic interactions are present. Results of fitting the Curie-Weiss law in the high temperature range are presented in Table 6.2.
The observed values for $p_{\text{eff}}$ of the Ni-based hybrids are close to theoretical spin-only value of $p_{\text{eff}}=2.8\mu_B$ for Ni$^{2+}$ (Table 6.2). Only NiCl$_3$(AN)$_2$ shows a different value caused by noisy data in this range, resulting in $p_{\text{eff}}=3.1\mu_B$. The low-temperature behavior shows additionally paramagnetic contributions, which can be explained by the magnetic response of finite length spin chains with an odd number of spins. These odd segments appear as paramagnetic contributions at low temperature. A smaller average length of the chains in the synthesized crystals implies a larger number of odd-length chains. The length of the chain is different from compound to compound and is set by the organic moiety and synthetic conditions.

Thermodynamically, one dimensional magnetic systems have no long-range order at finite temperature. This was proven by Mermin and Wagner for Heisenberg and XY chain systems\textsuperscript{16}. Thus, only short-range interactions dominate and the system entropy should be considered. In this case, we observe a broad maximum of the temperature dependence of the susceptibility along the chain. This maximum appears at a temperature of approximately 1.3 times the in-chain exchange interaction. Figure 6.2a displays characteristic features of the magnetic susceptibility for antiferromagnetic Heisenberg spin chain system. The Hamiltonian of this spin-system cannot be solved exactly, but a numerical approximation of the magnetization is given by the Weng equation (Eq. 3.3).
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\[
\chi = \frac{N\mu_B^2 g^2}{kT} \left( \frac{2 + 0.012\alpha + 0.777\alpha^2}{3 + 4.346\alpha + 3.232\alpha^2 + 5.834\alpha^3} \right)
\]

Where \( \alpha = \frac{\mu_1}{k_B T} \), and is only valid for an antiferromagnetically coupled isotropic spin. If we scale the maximum of the susceptibility in the Weng equation, we can fit the measured curves and extract the magnetic exchange constants \((J/k_B)\). The resulting values are presented in Table 6.2.

6.4 Discussion

To confirm the same nature of the magnetic behavior for all Ni-based compounds, the magnetic susceptibility curves of all Ni-based hybrids, normalized to the one-dimensional maximum values presented in Fig. 6.4. The normalized magnetization curves overlap. Therefore, we conclude that all hybrids represent one-dimensional spin-1 chains with variations in \( J \).
Let us now compare the influence of the structure variations, introduced by the organic moieties, on the magnetic behavior of the compounds. The observed values $J/k_B$ are plotted versus the in-chain Ni-Ni distance in Figure 6.5. We can approximate $J/k_B$ versus the in-chain Ni-Ni distance with a linear relation. Obviously, the Ni-Ni interaction depends on the direct Ni-Ni overlap as well as the Ni-Cl-Ni superexchange interactions, which both depend on the Ni-Ni distance.

The Ni$^{2+}$ spins couple antiferromagnetically in inorganic NiCl$_6$-chains. Antiferromagnetic (AFM) coupling is common for face-sharing NiCl$_6$ chains$^{11,17-21}$. The Ni-Ni exchange pathway introduces an AFM spin interaction which dominates the ferromagnetic interaction, mediated by Ni-Cl-Ni bond. We did not observe a Ni-Cl-Ni angle dependence of the exchange constant $J$. Therefore, we propose that changes of the in chain exchange constant $J$ occur via tuning of the AFM interaction. In the Ni-hybrids the NiCl$_6$ octahedra have a different distortion, which leads to changes in the Ni-Ni distance. This results in different intra-chain magnetic exchange constants.

Figure 6.4. Magnetization versus temperature for all NiCl$_3$-hybrids normalized to the maximum value.
Deviations from classical 1D magnetic behavior

Interestingly, we find an anomalous behavior for NiCl$_3$(PEA)$_2$ compound at low temperatures. In S=1 one-dimensional systems, deviations from classical Bonner-Fisher behavior can occur. There are two possibilities: a non-magnetic singlet ground state, described by Haldane, can appear at low temperature. In our compounds we find no evidence for Haldane behavior. Alternatively, long range order at low temperatures occurs in quasi one-dimensional systems due to weak finite inter-chain coupling. For example, Ishida et al. observed inter-chain coupling in [Co(hfac)$_2$*AnNN], leading to 3-dimensional order below 10K$^{22}$. Below the 3d-ordering temperature a large anisotropy of the magnetic susceptibility is observed, signaling magnetic order. In our hybrids, long-range order is obscured by paramagnetic contributions, which we ascribe to odd-length spin-segments$^{15}$.

Figure 6.5 shows magnetization versus temperature for the NiCl$_3$(PEA)$_2$ hybrid. The clearly observable deviation from the classical 1d behavior...
represented by a peak at around 8K is assigned to a magnetic transition. This phenomena was first discovered by A. Arkenbout in her doctoral thesis\textsuperscript{23}.

![Graph showing magnetization versus temperature](image)

**Figure 6.6.** Magnetization versus temperature dependence of NiCl$_3$(PEA)$_2$ hybrid.

Magnetizations versus temperature measurement at high field reveals disappearance of the peak and signal an ordered state at low temperatures, which does not follow Curie-Weiss law (Figure 6.7, upper curve).
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Figure 6.7. Magnetization versus temperature dependence of NiCl$_3$(PEA)$_2$ hybrid, measured at 0.5 T (lower curve) and 6T (upper curve).

Figure 6.8. Magnetization versus temperature dependence of NiCl$_3$(PEA)$_2$ hybrid, measured at 0.5 T parallel (upper curve) and perpendicular (lower curve) to the chain direction (with denoted values of maximum $\mu_B$/f.u. values).
To further confirm the existence of long-range order in the NiCl$_3$(PEA)$_2$ anisotropic measurements were performed (Figure 6.8).

The anisotropic character of the magnetization below 8K suggests a long-range magnetic state. 3d order can appear in magnetic chains system only in the presence of an inter-chain coupling or anisotropy$^{24}$. Let us now consider the Ni-Ni distances between the chains (Fig. 6.3b), where one can notice that NiCl$_3$(PEA)$_2$ has one of the smallest chain-chain distance of 6.88 Å and the highest $J/k_B$ value of the series.

![Figure 6.9](image)

**Figure 6.9.** μSR measurement of NiCl$_3$(PEA)$_2$ hybrid, performed in the range 2-8K. Solid lines display measured data, symbols display obtained fits.

To confirm the presence of 3d order in the hybrid, muon spectroscopy was used, with the μSR technique. Measurement of pressed powder of NiCl$_3$(PEA)$_2$ was performed at the ISIS-Riken muon facility in the range 2-8K with A.Nugroho and I.Watanabe. Figure 6.9 shows the temperature dependence of ZF-μSR spectra of NiCl$_3$(PEA)$_2$. The spectra show clearly the muon spin rotation which confirms that the system has a 3D long range order. The spectra were fitted using a damped oscillating function:
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\[ A(t) = A_0 \exp(-\lambda t)\cos(\gamma Bt + \phi), \]  

where $A_0$, $\lambda$, $B$, and $\phi$ are the asymmetry, the relaxation rate, the internal magnetic field, and the phase, respectively. $\gamma$ is the gyromagnetic ratio of the muon. The best fit of the spectra by using equation 6.4 were plotted in the continuous line. The temperature dependence of the asymmetry, the relaxation rate and the internal magnetic field obtained from the fitting are plotted in Fig. 6.10.

The temperature dependence of the internal magnetic field show a clear magnetic transition around 8K. This transition is also marked by the change of the asymmetry as well as the relaxation rate. It is noted that below the magnetic ordered state the relaxation rate is still finite. This indicate that there an inhomogeneous internal magnetic field in the ordered state which might due to the termination of the one-dimensional chain.
Figure 6.10. Temperature dependence of the asymmetry (a), the relaxation rate (b) and the internal magnetic field (c) obtained from the fitting of the μSR data.
6.6 Conclusion

In this chapter, structural dependences and magnetic properties of several Ni-based organic-inorganic hybrids were studied. We revealed the strong influence of the organic part of the hybrids on the structure of the inorganic NiCl$_3$ chains.

In conclusion, we present a variety of new Ni-based organic-inorganic hybrid compounds, which represent quasi one-dimensional spin chains. Their magnetic behavior corresponds with antiferromagnetic S=1 Heisenberg spin chains. We show that change of the organic moiety introduces structural changes in the chain forming inorganic NiCl$_6$ face-sharing octahedra. The Ni-Ni distance determines the exchange constant. It is determined by the requirement of commensurate lattices of the inorganic NiCl$_3$ chain and the organic herringbone block. Variations in this distance influence also the inter-chain distance. These systems offer the opportunity to systematically change the magnetic properties of quasi 1-dimensional magnetic spin chains by using different organic moieties. We also demonstrated three-dimensional magnetic order in NiCl$_3$(PEA)$_2$ hybrid below 8K and discussed its origin.
References


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