The Role of Tetrahedral Building Blocks in Low-Dimensional Oxohalide Materials

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Cover: Representation of a tube in the compound Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$. 

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Abstract

The structural architecture found in low-dimensional materials can lead to a number of interesting physical properties including anisotropic conductivity, magnetic frustration and non-linear optical properties. There is no standard synthesis concept described thus far to apply when searching for new low-dimensional compounds, and therefore control on the design of the new materials is of great importance.

This thesis describes the synthesis, crystal structure and characterization of some new transition metal oxohalide compounds containing p-elements having a stereochemically active lone-pair. First row transition metal cations have been used in combination with Se\textsuperscript{IV}, Sb\textsuperscript{III} and Te\textsuperscript{IV} ions as lone-pair elements and Cl\textsuperscript{−} and Br\textsuperscript{−} as halide ions. The lone-pairs do not participate in covalent bonding and are responsible for an asymmetric one-sided coordination. Lone-pair elements in combination with halide ions have shown to be powerful structural spacers that can confine transition metal building blocks into low-dimensional arrangements. The halide ions and lone-pairs reside in non-bonded crystal volumes where they interact through weak van der Waals forces. The transition metal atoms are most often arranged to form sheets, chains or small clusters; most commonly layered compounds are formed.

To further explore the chemical system and to separate the transition metal entities even more the possibility to include tetrahedral building blocks such as phosphate-, silicate-, sulphate- and vanadate building blocks into this class of compounds has been investigated. Tetrahedral building blocks are well known for their ability of segmenting structural arrangements by corner sharing, which often leads to the formation of open framework structures. The inclusion of tetrahedral building blocks led to the discovery of interesting structural features such as complex hydrogen bonding, formation of unusual solid solutions or faulted stacking of layers.

Compounds for which phase pure material could be synthesized have been characterized in terms of their magnetic properties. Most compounds were found to have antiferromagnetic spin interactions and indications of magnetic frustration could be observed in some of them.
List of publications

This thesis is based on the following publications referred to by the Roman numerals I-X in the text. These papers are listed in full at the end of the thesis.

I. Synthesis, crystal structure and magnetic properties of the open framework compound \( \text{Co}_3\text{Te}_2\text{O}_2(\text{PO}_4)_2(\text{OH})_4 \)
Iwan Zimmermann, Reinhard K. Kremer and Mats Johnsson,
Contribution: Synthesis, structural characterization, preliminary magnetic measurements, writing part of the manuscript.

II. Crystalline Iron Oxohalide Nanotube Pea Pods
Iwan Zimmermann, Mats Johnsson, Sven Lidin,
Contribution: Synthesis, magnetic measurements, part of the structural characterization, writing part of the manuscript.

III. Crystal structure and magnetic properties of \( \text{Cr}_3\text{Te}_5\text{O}_{13}\text{Cl}_3 \)
Contribution: Synthesis, structural characterization, preliminary magnetic measurements, writing part of the manuscript.

IV. Synthesis and Crystal Structure of the Solid Solution \( \text{Co}_3(\text{SeO}_3)_{3x}(\text{PO}_3\text{OH})_4(\text{H}_2\text{O}) \) Involving Crystallographic Split Positions of \( \text{Se}^{4+} \) and \( \text{P}^{5+} \)
Iwan Zimmermann and Mats Johnsson,
Contribution: Structural characterization, magnetic measurements, writing part of the manuscript.

V. Two isostructural layered oxohalide compounds containing \( \text{Mn}^{2+} \), \( \text{Te}^{4+} \) and \( \text{Si}^{4+} \); crystal structure and magnetic susceptibility
Iwan Zimmermann, Reinhard K. Kremer and Mats Johnsson,
Contribution: Synthesis, structural characterization, writing part of the
manuscript.

VI. Stacking faults in a layered cobalt tellurium phosphate oxochloride
Iwan Zimmermann and Mats Johnsson,
Submitted for publication
Contribution: Synthesis, structural characterization, writing part of the manuscript.

VII. A Synthetic Route toward Layered Materials: Introducing Stereochemically Active Lone-Pairs into Transition Metal Oxohalides
Iwan Zimmermann and Mats Johnsson,
Contribution: Synthesis, structural characterization, writing part of the manuscript.

VIII. Synthesis and Crystal Structure of the Iron(III) Oxotellurate(IV) Phosphate Oxide Chloride \( \text{Fe}_{11}(\text{TeO}_3)_2(\text{TeO}_4)_3(\text{PO}_4)_2\text{O}_4\text{Cl}_3 \)
Iwan Zimmermann and Mats Johnsson,
Contribution: Synthesis, structural characterization, writing part of the manuscript.

IX. Synthesis, crystal structure and magnetic properties of a new antimony sulphate oxide \( \text{CuSb}_{6}(\text{SO}_4)_2\text{O}_8 \)
Iwan Zimmermann, Reinhard K. Kremer and Mats Johnsson,
Submitted for publication
Contribution: Synthesis, structural characterization, writing part of the manuscript.

X. Synthesis and crystal structure of \( \text{Mn}_3\text{Sb}_{2+x}(\text{VO}_4)_{2-x}\text{O}_{2+3x}\text{Cl}_2 \) \((0.08 < x < 0.13)\), a vanadium oxochloride with a \( \text{V}^V – \text{Sb}^{III} \) split position
Iwan Zimmermann and Mats Johnsson,
Submitted for publication
Contribution: Synthesis, structural characterization, writing part of the manuscript.

Papers outside the scope of this thesis:

The synthetic cobalt vanadium selenite, \( \text{Co}_2\text{V}_2\text{Se}_2\text{O}_{11} \)
Faiz Rabbani, Iwan Zimmermann and Mats Johnsson,
Synthesis, Crystal Structure and Thermal Decomposition of the New Cadmium Selenite Chloride, Cd₄(SeO₃)₂OCl₂

**Cobalt selenium oxohalides: catalysts for water oxidation**

**Synthesis and crystal structure of a series of incommensurately modulated composite oxohalide compounds**
Iwan Zimmermann, Alexis Corgnet, Mats Johnsson and Sven Lidin, *Dalton Trans.* in print. DOI: 10.1039/C4DT02084G.
# Contents

Abstract ............................................................................................................................................... v

List of publications .......................................................................................................................... vii

1. Introduction ...................................................................................................................................... 1
   1.1 Low-dimensional materials ........................................................................................................ 2
       1.1.1 Low-dimensional nanomaterials ........................................................................................ 2
       1.1.1 Low-dimensional arrangements in solids .......................................................................... 3
   1.2 Structural building blocks ........................................................................................................... 7
       1.2.1 Tetrahedral building blocks ............................................................................................... 8
       1.2.2 Lone-pair ions ................................................................................................................... 9
   1.3 Chemical bonding ...................................................................................................................... 12
   1.4 Physical properties .................................................................................................................... 13
       1.4.1 Non-centrosymmetric compounds ...................................................................................... 14
       1.4.2 Multiferroic properties ..................................................................................................... 15
       1.4.3 Magnetic frustration ......................................................................................................... 15
       1.4.4 Catalytic properties .......................................................................................................... 17
       1.4.5 Bond valence sum calculations ........................................................................................ 18
   1.5 Aim and Scope .......................................................................................................................... 21

2. Experimental ..................................................................................................................................... 23
   2.1 Synthesis ..................................................................................................................................... 23
       2.1.1 Chemical reactions in evacuated silica tubes ..................................................................... 25
       2.1.2 Hydrothermal synthesis .................................................................................................... 26
   2.2 Characterization ........................................................................................................................ 28
       2.2.1 Single crystal X-ray diffraction (SXD) ............................................................................. 28
       2.2.2 X-ray powder diffraction (PXRD) ..................................................................................... 28
       2.2.3 Scanning electron microscopy (SEM) ............................................................................... 29
       2.2.4 Physical property measurement system (PPMS) ............................................................... 29
       2.2.5 Thermogravimetry (TG) .................................................................................................. 29
       2.2.6 Infrared Spectroscopy (IR) ............................................................................................... 29

3 Results and Discussion .................................................................................................................. 31
   3.1 Layered Trm-Lp-O-X compounds .............................................................................................. 33
   3.2 Structures with tetrahedral building blocks ................................................................................ 35
       3.2.1 Tubular units in Fe$_7$Sb$_3$(PO$_4$)$_3$O$_8$X$_3$ (X=Cl, Br) ...................................................... 35
3.2.2 Layered Co$_2$Te$_3$(PO$_4$)$_6$Cl, CuSbO$_6$(SO$_4$)$_2$ and Mn$_4$(TeO$_3$)(SiO$_4$)X$_2$
(X=Br,Cl) ...........................................................................................................37
3.2.3 Open framework structures ........................................................................38
3.3 Solid solutions: Split positions involving a lone-pair element .................40
3.4 Hydrogen bonding .........................................................................................42
3.5 Diffuse scattering due to faulted stacking of layers ...............................44
3.6 Magnetic measurements ..............................................................................45
  3.6.1 High temperature magnetic properties ..................................................46
  3.6.2 Low temperature magnetic properties ....................................................47
4. Summary and Conclusion .............................................................................49
5. Populärvetenskaplig Sammanfattning .........................................................53
6. Acknowledgements .........................................................................................55
7. References .......................................................................................................57
1. Introduction

The arrangement of structural building blocks at the atomic level is of great importance in all crystalline materials as it directly relates to the physical properties. The easiest way of describing the connectivity of atomic building units in a crystal structure is in terms of its dimensionality. Structures with low-dimensional arrangements have shown exceptional properties such as frustrated magnetism or anisotropic conductivity.\(^1\)\(^-\)\(^2\) In transition metal oxides and oxohalides it is the arrangement of the transition metals that is of special interest because these elements are mostly responsible for the physical properties. To reduce the dimensionality of such compounds p-elements having a stereochemically active lone-pair such as Se\(^{4+}\), Sb\(^{3+}\) Te\(^{4+}\), Bi\(^{3+}\) or I\(^{5+}\) can be introduced into the crystal structure. Due to their non-bonding electron pair, such elements adopt a one-sided, asymmetric coordination caused by a second order Jahn Teller (SOJT) distortion.\(^3\)\(^-\)\(^4\) Lone-pairs do not participate in bonding, and therefore their terminating properties help to open up the crystal structure; this effect is sometimes referred to as “chemical scissors”.\(^5\)\(^-\)\(^6\) Structures observed within this class of compounds are often layered with transition metal oxide nets in the middle of the extended 2D sheets, to which the lone-pair elements and halide atoms are attached and protrude from the layers, allowing weak van der Waals interactions to be present along the stacking direction. Structural examples are e.g. Co\(_2\)TeO\(_3\)X\(_2\) (X=Cl,Br)\(^7\) or Cu\(_3\)Bi(To\(_3\))\(_2\)O\(_2\)Cl\(^8\). In the latter, the Cu atoms are arranged in a two-dimensional kagome lattice. In some cases the dimensionality of the arrangement of the transition metals is further reduced, and one-dimensional chain arrangements, as in CaCo\(_2\)Te\(_3\)O\(_8\)Cl\(_2\)\(^9\) or even clusters as in FeTe\(_2\)O\(_3\)X (X=Cl,Br),\(^10\) are observed.

Other structural units, which are well known for their ability to form open framework structures, are tetrahedral building blocks such as phosphates, silicates or sulphates.\(^11\) Due to their ability to connect different building blocks through mainly corner sharing, they exhibit a rich and interesting structural chemistry.\(^12\)\(^-\)\(^14\) By including tetrahedral building blocks into transition metal oxides, and oxohalides having a stereochemically active lone-pair present, a new class of compounds opens up with potentially interesting structural and physical properties. Up until now only a few such compounds are known and most of them are oxides. Examples are A\(_2\)TeMo\(_2\)O\(_6\)(PO\(_4\))\(_2\) (A = K, Rb, Tl, Cs)\(^15\), BaMTeO\(_3\)(PO\(_4\)), M= Nb, Ta\(^16\) or the minerals chapmanite Fe\(_2\)Sb(SiO\(_4\))\(_2\)(OH)\(^17\) and nabokoite Cu\(_7\)TeO\(_4\)(SO\(_4\))\(_5\)·KCl.\(^18\)
The aim of this thesis is to investigate new layered structures within the Lp-Trm-O-Cl (Lp = lone-pair element, Trm = transition metal) system in terms of structural chemistry and physical properties and to try to incorporate additional tetrahedral building blocks into this class of compounds.

1.1 Low-dimensional materials

In materials with reduced dimensionality the atoms or structural building blocks are, for example, arranged in layers, tubes or clusters. Low-dimensional materials can be nano sized single units (nano materials) with highly anisotropic arrangements or macroscopic materials having a low-dimensional structure architecture. In both cases the confinement of structural building blocks into well-defined low-dimensional arrangements can lead to interesting structural and physical properties.

1.1.1 Low-dimensional nanomaterials

During the last few decades considerable attention has been focused on low-dimensional nanomaterials, especially on the different allotropes of carbon and carbon analogous materials.[19-21] A nanomaterial consists of a single unit whose size is in the range of ~100 nm or lower in at least one dimension. Graphene is a single layer of graphite where the sp² hybridized carbon atoms arrange in hexagonal honeycomb nets. Rolling these planar nets up into cylinders and spheres results in carbon nanotubes and bucky balls, which are called fullerenes. Due to the confinement of electrons in these carbon allotropes along 2 (graphene), 1 (nano tube) and 0 (bucky ball) dimensions these materials have interesting properties, which are very different from the ones observed in bulk materials cf. diamond.

![Graphene and Carbon Nanotubes](image)

**Figure 1.1** Density of states (DOS) for: (a) 3D material (diamond), (b) 2D material (graphene), (c) 1D material (carbon nanotubes), (d) 0D material (bucky ball).

Graphene and carbon nanotubes have gained considerable attention due to their high mechanical strength and interesting electrical and optical proper-
ties. This behavior can be explained by looking at the distribution of the density of states (DOS) in the material (Figure 1.1). In a 3D material the DOS are a continuous function of energy, while in 2D the DOS can be described as a step function. In the one-dimensional case the DOS shows distinct maxima, which are called van Hove singularities.[22] In a 0D system with Quantum dots, DOS are only found at certain energies.

1.1.1 Low-dimensional arrangements in solids

The most simple and straightforward way of describing any periodic solid-state material is to look at its crystal structure. Physical properties strongly depend on how the material is built at an atomic scale and how individual atoms interact with each other. Although the crystal structure of a compound is always three-dimensional, as it describes the position of the atoms in space, certain building units within the structure can adopt a lower dimensional arrangement. Figure 1.2 shows possible arrangements of building blocks concerning the example of corner sharing MO_6 octahedra. Connecting the octahedra in all possible directions will result in (a) a 3D framework, (b) in two directions will give 2D layers, (c) in one direction gives 1D chains (d) and only few individual connected octahedra give 0D cluster arrangements.

Figure 1.2  Arrangement of structural building units into (a) 3D framework, (b) 2D layers, (c) 1D chains and (d) 0D clusters. The building units are represented as corner sharing MO_6 octahedra.
Reducing the dimensionality of a material often results in an increase of its anisotropy, giving the material interesting physical properties. In many cases it is the transition metal ions that are of special interest because they are mainly responsible for the physical properties of the material. Their d-electrons can give rise to *e.g.* optical, magnetic or electrical properties. The arrangement of the transition metal ions within the crystal structure is therefore of paramount importance. A low-dimensional arrangement of atoms is not always very favorable, especially for ionic compounds, as sphere shaped ions tend to close pack and fill the crystal space in order to become as dense as possible. A way to avoid this problem is to introduce suitable building blocks that can act as spacers in the structure and help to separate the desired atoms into a low-dimensional arrangement. In metal organic compounds simple organic molecules such as carboxylic acids, amines or nitrides can coordinate with the transition metals and act as spacers. Figure 1.3a shows the structure of the ferrimagnetic single molecular magnet cluster $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ ($\text{dpm}=2,2,6,6$-tetramethylheptane-3,5-dionate). The core of the cluster consists of four edge sharing $[\text{FeO}_6]$ octahedra with which the organic ligands are coordinated. Due to the bulky organic terminal ligands the transition metal core is well isolated. Neighboring clusters are connected by weak van der Waals interactions. Figure 1.3b shows the layered coordination polymer $[\text{Mn}^{\text{II}}_2(\text{cis-1,2-chdc})_2]$ (cis-1,2-chdc=cis-cyclohexane-1,2-dicarboxylate).

![Figure 1.3](image.png)

*Figure 1.3* Low-dimensional arrangements in inorganic-organics hybrid materials. (a) tetrairon single molecular magnet cluster; (b) layered coordination polymer.

The manganese oxide polyhedra build up a two-dimensional net with which the organic ligands are coordinated. Through this each layer is well separat-
ed from the next one. The layers are held together by van der Waals interactions.

An interesting class of compounds that have low-dimensional arrangements are polyoxometalates, which are known for their ability of forming large cluster arrangements. Polyoxometalates are built from self-assembling [MO₆] polyhedra, where M is a transition metal belonging to group 5 or 6 with a high oxidation state such as V⁵⁺, Mo⁵⁺ or W⁶⁺.[25] Normally, additional building blocks, such as phosphate or silicate groups, are also present. In most cases polyoxometalates are anions and charge balance is achieved by cations located around the clusters or in the pores of the clusters. Figure 1.4 shows the crystal structure of the Preyssler anion,[26] [NaP₅W₃₀O₁₁₀]⁴⁻ built from 30 [WO₆] octahedra and 5 [PO₄] tetrahedra and a Na⁺ in the cluster pore. An example of a compound containing the Preyssler anion is e.g. (NH₄)₁₄NaP₅W₃₀O₁₁₀·31H₂O, which can be used as an ion exchanger.[27]

Figure 1.4 Structural model of the Preissler anion[26] [NaP₅W₃₀O₁₁₀]⁴⁻ built up from 30 [WO₆] octahedra (blue) and 5 [PO₄] tetrahedra (orange). The Na⁺ ion (green) is located in the cluster pore.

Another very common way of forcing transition metal oxides to take lower dimensional arrangements is the use of additional well-defined building blocks such as phosphate, silicate or sulphate groups. Figure 1.5a shows the structure of LiFePO₄, which is used as cathode material in batteries.[28] The phosphate groups connect to the [FeO₆] octahedra and separate them into layers. The lithium ions are located in small channels in between the layers for charge balance. Suitable building blocks are also ”inert” transition metals such as V³⁺, that has an empty d-electron shell or Zn²⁺ for which the d-electron shell is completely filled. An example is the compound Cu₃Zn(OH)₆Cl₂,[29] where the diamagnetic zinc atoms separate the copper
ions to lay on a well-defined kagome net, which leads to magnetic frustration in this compound.

Figure 1.5 (a) Layered crystal structure of LiFePO$_4$\cite{28} and (b) FeCl$_2$\cite{30} with the iron atoms arranged within the layers separated by phosphate and chlorine building units, respectively.

Halide ions are very common terminal ligands that can act as spacers and many simple transition metal halides or oxohalides have a layered crystal structure where the halide ions are protruding from the layers. Figure 1.5b shows an example of a simple transition metal chloride FeCl$_2$.\cite{30} The layer coherence is given by weak chlorine-chlorine interactions.

In this thesis the focus lies on using p-elements having a stereochemically active lone-pair as a spacer. The lone-pair does not participate in any bonding and it acts as a terminal ligand, which occupies empty voids in the crystal space. As a result the lone-pairs can act as “chemical scissors” that are able to cut down the dimensionality of a structural arrangement and often layered compounds are observed. An example of this is the copper selenium oxochloride Cu$_3$(SeO$_3$)$_2$Cl$_2$.\cite{31} Each layer consists of an extended transition metal oxide net, to which the lone-pair elements and the halide ions are attached, see Figure 1.6. The lone-pairs (black spheres) and the halide ions (green spheres) are protruding from the layers, and weak van der Waals forces from lone-pair-halide interactions ensure layer coherence. This arrangement does not necessarily happen due to strong lone-pair or halide interactions, as van der Waals forces are only weak, but can be explained as a consequence of the lone-pairs and halide ions being excluded from crystal bonding interactions.
Layered crystal structure of Cu$_3$(SeO$_3$)$_2$Cl$_2$.[31] The transition metal oxide net is sandwiched by the lone-pair elements and the halide ions. Weak lone-pair-halide interactions are indicated by orange circles.

1.2 Structural building blocks

Figure 1.7 shows the periodic table, and the elements utilized in this thesis are highlighted. The design of lone-pair based low-dimensional materials having potentially interesting physical properties is based on the combination of different building blocks. Elements from the p-block with a np$^0$s$^2$ electron configuration are the source of the stereochemically active lone-pair, which together with the halide ions are supposed to open up the crystal structure and form low-dimensional arrangements. It is the transition metals that give a compound its magnetic properties if unpaired d-electrons are present. To open up structures even more, and to create structural variety, additional well-defined tetrahedral building blocks such as phosphate or sulphate groups can be included. Similar behavior is observed for transition metals having a d$^0$ or d$^{10}$ electron configuration. In this work metal oxides and metal halides, where the metal cations are in the desired oxidation state, have been used as starting materials during synthesis.
1.2.1 Tetrahedral building blocks

Due to their relatively small size p-elements from the 2\textsuperscript{nd} or 3\textsuperscript{rd} period at their highest oxidation state preferably take a tetrahedral coordination. The tetrahedra are usually very regular with only minor distortions and can be regarded as being inert, as they have no unpaired electrons present. Very similar behavior can be observed with transition metals having either a d\textsuperscript{0} or d\textsuperscript{10} electronic configuration, some transition metal cations such as Zn\textsuperscript{2+} or V\textsuperscript{5+} can also have tetrahedral coordination with regular building units, but due to their larger size higher coordination numbers are also observed. Tetrahedral units are interesting from a structural point of view as such building blocks tend to form open framework structures due to only corner sharing; edge or face sharing are unlikely because the highly charged cations are then coming to close to each other. Figure 1.8 shows tetrahedral building blocks utilized in this thesis with average bond lengths calculated from BVS values.

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**Figure 1.7** Periodic table of elements: s-block (grey), p-block (orange), d-block (blue). Elements used in this thesis are highlighted. F-block elements are not shown.

**Figure 1.8** Examples of tetrahedral building blocks and their average bonding distance.
1.2.2 Lone-pair ions

A ns^2np^0 electron configuration in p-block elements can result in very distorted coordination geometries due to the presence of a stereochemically active lone-pair (E). E is a non-bonding electron pair, which does not allow for connecting with further atoms and occupies non-bonded space in the crystal structure. Elements having stereochemically active lone-pairs are e.g. Tl⁺, Pb⁴⁺, Sn³⁺, Sb³⁺, Se⁴⁺, Te⁴⁺, I⁵⁺. The electronic repulsion of the lone-pair electrons towards bonded anions gives rise to an asymmetric one-sided coordination behavior of the metal cations. E can be described as a terminal ligand bonded to the cation center and calculations have shown that its size is comparable to that of an oxygen or a fluorine atom. However the cation-lone-pair distance is much shorter than the cation-anion distance. In the literature different ways of representing the stereochemically active lone-pair are discussed as shown in Figure 1.9.

![Different representations of the stereochemically active lone-pair. Two dots, a black sphere, orbital shaped cone, hollow semisphere (from left).](image)

The most common way of indicating the lone-pair is by two dots but also representations as a small sphere, an orbital shaped cone or a hollow semisphere can be found. The electron density of a lone-pair is not localized at a central point, as is a normal atom, but can be better described as laying on a crescent shaped isosurface around the cation that can be calculated from the electron localization function. Its position can therefore not be determined by standard X-ray crystallographic experiments. A way of indicating the stereochemically active lone-pair in the crystal structure is to add a black dummy atom, E, so that the lone-pair cation is located at the bary-center of the polyhedron; an evaluation of average distances in between lone-pair elements and E for a number of compounds has been made by Galy. The bonding around lone-pair cations can then be visualized by drawing coordination polyhedra including the stereochemically active lone-pair. Due to the short distance in between a lone-pair cation and E the polyhedra may be rather distorted. Depending on the number of ligands e.g. tetrahedra (ML₃E), trigonal pyramids (ML₄E) or octahedra (ML₅E) can form (Figure 1.10).
Lone-pair elements can have very different coordination arrangements depending on the charge, the ionic radius, the ligands and the chemical environment they are exposed to. The lone-pair effect is normally more pronounced with ligands which are less electronegative. In many halide compounds, such as TeCl$_4$ where tellurium has a distorted octahedral coordination, the distortion caused by the lone-pair is less pronounced.$^{[35]}$ In systems containing oxygen ions, the coordination of lone-pair elements towards halide ions is very rare and therefore the focus in this thesis is on coordination with oxygen. The size of the lone-pair cation is important for the maximal number of ligands it can accept. For example, the relatively small Se$^{4+}$ cation is a very rigid building block and only [SeO$_3$E] tetrahedra with well-defined bond lengths and bond angles are observed when coordinated with oxygen. An example is SeO$_2$ where the [SeO$_3$E] tetrahedra are connected in one-dimensional chains via corner sharing.$^{[36]}$ In fact, tetrahedral coordination is the most common bonding among lone-pair cations. The larger Sb$^{3+}$ is more flexible and [SbO$_4$E] trigonal bipyramids are also found and for Te$^{4+}$ and Tl$^{+}$ even five coordination can be observed. Due to the larger size elements of the 6th period, Tl$^{+}$, Pb$^{2+}$ or Bi$^{3+}$ behave more like alkali metals and high coordination numbers can be observed. Relativistic effects in those heavy elements lead to a reduced interaction between cation s and anion p states, which results in less pronounced lone-pair distortions among those elements. Tl$^{+}$, for example, can either have a completely symmetrical coordination or show a lone-pair distortion (Figure 1.11).

*Figure 1.10* Coordination polyhedra found around lone-pair elements including the stereochemically active lone-pair by a black dummy atom E. (a) Distorted tetrahedra, (b) trigonal pyramids and (c) octahedra can be observed.
Figure 1.11 Overview of different coordination behavior towards oxygen (O) for p-elements (L) having a stereochemical lone-pair present.

The origin of the distortion in lone-pair elements is often explained by a second order Jahn Teller effect (SOJT). While the first order Jahn Teller effect shows distortion due to a degenerate electronic ground state, as observed in e.g. Cu$^{2+}$,[37] the SOJT occurs due to interactions with a non-degenerate ground state with a low lying exited state. This phenomena is widely observed in d$^0$ transition metals due to a small energy gap between the lowest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). With transition metals the distortions are rather small and occur along faces, edges or corners of the metal cation polyhedron.[38] In lone-pair elements, HOMO and LUMO are assigned to the non-bonding s$^2$ and p$^0$ orbitals of the lone-pair cation. The total energy of the system is reduced by on site s-p mixing (hybridisation), which results in a lowering of symmetry and thus very distorted coordination environments. This theory was introduced by Orgel in the 1950’s,[39] and recently more advanced models were developed to explain more clearly why the lone-pair is not always stereochemically active. Recent studies suggest that the s$^2$ electrons are not "inert", but their interaction with the anion p states is of significant importance. This has been shown based on density functional theory (DFT) calculations.[4] An s-p interaction will create bonding and antibonding orbitals (Figure 1.12). Through hybridization between the empty cation p and antibonding s-p orbitals, a stabilization of the occupying electronic states can be achieved. This will lead to a distortion of the coordination geometry.
similar to what is described above.\(^{[40]}\) Because the anion cation interaction plays a major role in this model, the lone-pair effect should be more pronounced with metals and ligands whose anion p and cation s states have a close energy level.

**Figure 1.12** Energy level diagram describing the formation of stereochemically active lone-pairs. L is a p-element cation with the period n. The closer in energy the O 2p states are compared to the L ns states the more stereochemically active the lone-pair effect is.

### 1.3 Chemical bonding

The way atoms connect within the crystal structure is of great importance as it will affect the arrangement of different building blocks in the material and thus the dimensionality. As discussed earlier, low-dimensional materials such as layered compounds are formed through the weak interactions of the lone-pairs and halide ions that reside in non-bonding volumes, while the transition metals are located in covalently bonded oxide nets in the layer middle. In order to get such an arrangement it is therefore important that lone-pair elements only bond toward oxygen atoms, ensuring a clear separation between the halide ions and lone-pairs in the structure. To understand the bonding situation within this class of compounds the simple rules of the Hard-Soft Acid-Base (HSAB) principle introduced by Pearson\(^{[41-42]}\) can be applied. In the HSAB concept, ions are classified as being either hard or soft acid-bases, depending on their polarizability. Hard acids and bases have a
high charge, small ionic radius and low polarizability in respect to soft acids and bases. Figure 1.13 shows typical lone-pair elements, transition metals and anions that are classified into hard, borderline and soft, according to values taken from Brown.\cite{Brown43} In this simplified model the HSAB parameters were estimated according to charge and the average coordination number of the different ions. Within the HSAB concept hard acids prefer to bond to hard base ions and soft acids form stronger bonds towards soft bases. Hard–soft interactions are, however, less favored. Most highly charged lone-pair elements and transition metals are hard acids that prefer to bond to the relatively hard oxygen anions, whereas transition metals and lone-pair elements with a low charge are soft and prefer to bond to the softer halide ions. Transition metal ions with a medium charge (+2) are borderline ions and form bonds to both oxygen and halide ions.

![Figure 1.13](image)

**Figure 1.13** Classification of different ions into hard, borderline and soft acid-bases. Highly charged lone-pair elements preferably bond to oxygen, whereas borderline transition metals can coordinate with either oxygen or halide anions.

### 1.4 Physical properties

The inclusion of lone-pair elements into the crystal structure has often been shown to result in low-dimensional arrangements of transition metal ions that can lead to interesting physical properties like geometrical frustration. On the other hand the one-sided, asymmetric coordination nature of lone-pair elements can be a main cause for the formation of non-centrosymmetric materials having a large dipole moment and thus showing *e.g.* non-linear optical (NLO) properties.
1.4.1 Non-centrosymmetric compounds

The properties of a material strongly depend on the symmetry of its crystal structure, and many interesting properties such as pyroelectricity, piezoelectricity, and non-linear optical properties can be found in non-centrosymmetric compounds. A compound is non-centrosymmetric if it does not have a center of inversion, thus \([x,y,z] \neq [-x,-y,-z]\). A non-centrosymmetric crystal structure belongs to one of the 21 acentric crystal classes and depending on the symmetry in the class, different properties can be observed in the compound.\(^{[44]}\) The non-centrosymmetric point groups can be separated into polar and non-polar groups (Figure 1.14). All non-centrosymmetric point groups except for 432 show piezoelectric and second harmonic generation (SHG) properties but only the ten polar groups are also pyroelectric.

**Polar**

\[ 1; 2; 3; 4; 6; m; mm2 3m; 4mm; 6mm \]

\( \text{Pyroelectric} \)

**Non-polar**

\[ -4; 422; 222; 622; 32; 23 -42m; -6; -43m; -62m 432 \]

**Piezoelectric. Second Harmonic Generation (SHG)**

**Figure 1.14** Summary of the 21 acentric point groups. Except for 432 all of them show piezoelectric and SHG properties but only the 10 polar groups are pyroelectric.

A search in the inorganic structural database (ICSD) shows that only around 20\% of all inorganic structures crystallize in a non-centrosymmetric space group. The procedure to obtain crystal structures that do not have an inversion center present is not often straightforward, but it has been shown that using highly asymmetric building blocks in the synthesis increases the possibility of finding non-centrosymmetric compounds. Therefore, many oxides that have cations with a SOJT distortion also have a non-centrosymmetric crystal structure. Cations susceptible to SOJT are either \(d^0\) transition metals such as, for example, \(V^{5+}\) in Na\(_3\)VO\(_2\)B\(_3\)O\(_{11}\),\(^{[45]}\) p-elements with a stereochemically active lone-pair such as Se\(^{4+}\) in Au\(_2\)(SeO\(_3\))\(_2\)(SeO\(_4\))\(^{[46]}\) or a combination of both as in RbSe\(_2\)V\(_3\)O\(_{12}\).\(^{[47]}\) A common way of characterizing non-centrosymmetric materials is to measure their piezoelectric or SHG properties. In many cases the structure will also be polar due to a dipole moment generated by the asymmetric coordination around the metal cation. A structural example is BaZnTe\(_2\)O\(_7\)\(^{[48]}\) where the Te\(^{4+}\) adopt a distorted seesaw coordination with the stereochemically active lone-pairs all pointing in a similar direction, which results in a net dipole moment along the layers (Fig-
ure 1.15). In this case pyroelectric measurements can also be performed. Not all structures having a distorted cation present are non-centrosymmetric or even polar. In most cases the lone-pairs arrange in a way so that they point towards each other leaving no net dipole moment.

![Figure 1.15](image)

**Figure 1.15** Single layer in BaZnTeO$_7$. [Zn$^{2+}$O$_4$] blue, [Te$^{6+}$O$_6$] dark grey, Te$^{4+}$ light grey, O$_2^-$ red. The individual dipole moments from the distorted [TeO$_4$] polyhedra are shown by blue arrows and the overall dipole moment in the layer is indicated by a green arrow.

1.4.2 Multiferroic properties

Multiferroics are materials that exhibit two ferroic properties simultaneously in a single phase.$^{[49-50]}$ The coexistence of ferromagnetism and ferroelectricity is for the most part addressed. The interaction between magnetically and electrically ordered states leads to interesting properties. Multiferroics have potential applications in e.g. new data storage devices, spintronics or magnetic sensors.$^{[51-52]}$ Despite their huge potential interest, only few materials are found to be multiferroic. The main reason for this is that most oxides showing magnetic properties due to their unpaired d-electrons contain the center of symmetry and do not allow electric polarization. On the other hand, most oxides showing ferroelectric properties do not have transition metals with unpaired d-electrons present. Introducing p-elements that have stereochemically active lone-pairs has been shown to be helpful in removing the centrosymmetry in magnetic transition metal oxides.$^{[53]}$ Examples where multiferroic behavior was observed due to a lone pair effect are e.g. BiFeO$_3$.$^{[54]}$ or BiMnO$_3$.$^{[55]}$ A strong coupling in between magnetic and electrical properties has been found in magnetically frustrated systems that show ferroelectricity.$^{[56]}$ An example is the geometrically frustrated oxohalide cluster compound FeTe$_2$O$_5$Br.$^{[57]}$

1.4.3 Magnetic frustration

In magnetism it is the topological arrangement of the spins, resulting from unpaired d-electrons, which determine the magnetic property of a material.
Neighboring spins located on a crystal lattice tend to strongly interact with each other and in most cases an antiferromagnetic ordering (antiparallel alignment) is realized to minimize the total energy of the system. An example of antiferromagnetic ordering is the compound BaNi$_2$V$_2$O$_8$\textsuperscript{[58]} where the spins (Ni atoms) that are located on a hexagonal honeycomb crystal lattice (Figure 1.16a) are aligned perfectly antiferromagnetically at low temperature, leading to a well-ordered ground state with no residual entropy of the spins. However, if the spins are located on e.g., a triangular lattice (see Figure 1.16b) it is not possible to align all the spins antiparallel and even at very low temperature the spins are not ordered giving a highly degenerate ground state.

![Figure 1.16](image)

**Figure 1.16** Different crystal lattices which (except (a)) lead to magnetic frustration. (a) Perfect antiferromagnetic arrangement in a hexagonal lattice, (b) trigonal lattice, (c) Kagome lattice, (d) Pentagonal Cairo lattice, (e) pyrochlore lattice.

The system is said to be geometrically frustrated and thus no long-range ordering of the spins is observed.\textsuperscript{[59]} This state is also described as a liquid spin state in analogy with an ordinary liquid in which the molecules form a dense, highly correlated state that has no static order.\textsuperscript{[60]} Magnetic frustration occurs in low-dimensional compounds such as clusters or layers but also 3D frustrated systems are known. Clusters of magnetically frustrated iron atoms are found for example in the oxohalide compound FeTe$_2$O$_5$X (X=Cl,Br).\textsuperscript{[7]} In layered compounds magnetic frustration is observed if the metal ions arrange
on a frustrated lattice such as e.g. a triangular lattice, a kagome lattice or a pentagonal Cairo lattice (see Figure 1.16c). Kagome lattices are fairly common and observed in e.g. Ba$_2$Sn$_2$Ga$_2$ZnCr$_7$O$_{22}$, whereas pentagonal lattices are rare due to the 5 fold symmetry, an example is Bi$_4$Fe$_5$O$_{13}$F. A frustrated 3D lattice is the pyrochlore lattice (Figure 1.16d), which is built by corner sharing tetrahedra and structures showing this arrangement are often called spin ice compounds. The reason for this is that disorder in this lattice was first described by the example of the hexagonal ice structure where the oxygen atoms are located in the center of the tetrahedra and the hydrogen atoms are disordered on the half occupied corners. The nature of the pyrochlore lattice prevents an ordering even at very low temperatures. A structural example is the compound Ho$_2$Ti$_2$O$_7$ where the Ho$^{3+}$ atoms are located on the pyrochlore lattice. An indication if a compound is magnetically frustrated can be obtained from the frustration parameter $f$ defined by Ramirez (Eq. 1.1).

$$f = \frac{-\theta_W}{T_c} \quad \text{(Eq. 1.1)}$$

where $\theta_W$ is the Weiss parameter and $T_c$ the magnetic transition temperature. Compounds having a value of $f$ larger than ten are considered to be strongly frustrated. An example of a highly geometrically frustrated compound is NaTiO$_2$ with $f > 500$.

### 1.4.4 Catalytic properties

The ever increasing global need of energy and shortening of natural energy resources such as oil has brought up the idea of converting solar energy into water splitting as a sustainable and environmental friendly solution to this problem. Both sunlight and water are abundant and renewable. The challenge has been to find suitable materials, which can act as efficient catalysts for water splitting through sunlight. Up to now only few semiconducting materials are known, which can catalyze the overall water splitting and most research is focused on half reactions (either water reduction or oxidation). To find suitable materials for the oxygen evolution from water oxidation seems to be the more difficult challenge but recently some layered materials having stereochemically active lone-pairs such as BiZn$_2$VO$_6$ and BiCu$_2$VO$_6$ have been found to be fairly efficient. Catalytic properties for water oxidation were also explored on two cobalt selenium oxohalide compounds: Co$_4$Se$_3$O$_6$Cl$_2$ and Co$_3$Se$_4$O$_{10}$Cl$_2$ which are 3D frameworks with small channels.
1.4.5 Bond valence sum calculations

In 1929 Linus Pauling published his work on the principles determining the structure of complex ionic compounds,\(^{[71]}\) which can be seen as the starting point of the bond valence model. Pauling stated that the charge of an anion is compensated by the sum of the electrostatic bond strengths surrounding it, which can be calculated from the cation charge and the coordination number. This concept was later on improved and instead of charge and coordination number the actual bond lengths were used as a measure of bond strength. Brown and his coworkers realized that the bond valence of a cation anion bond is best described by Eq. 1.2.\(^{[72]}\)

\[
\nu_i = e^{-\frac{R_0 - R_i}{B}} \quad \text{(Eq. 1.2)}
\]

\[
V = \sum \nu_i \quad \text{(Eq. 1.3)}
\]

This formula is purely empirical and depends on the experimental bond length \(R_i\) and on the parameters \(R_0\) and \(B\). It was found that \(B\) has a constant value of 0.37 for most inorganic compounds leaving \(R_i\) the only variable. Using the inorganic structural database (ICSD) \(R_i\) parameters were calculated from known structures and the values for various cations were tabulated by Brown.\(^{[73]}\)

\[\text{Figure 1.17} \quad \text{Bond valence of Te}^{4+}, \text{Cr}^{3+} \text{and P}^{5+} \text{bonded to oxygen as a function of bond length. The bond strength decreases exponentially with increasing bond length.}\]

Figure 1.17 shows the dependence of the bond length \(R_i\) and the bond valence for three different cations coordinated to oxygen. The curves mainly depend on the charge and the size of the cations. The range of a bond being
possible is rather narrow as with increasing length the BVS contribution decreases exponentially. On the other hand the minimal bond distance is limited by the repulsion of atoms coming to close to each other. The total valence of an atom is equal to its oxidation state and it can be obtained by summing the valences of all its bonds (Eq. 1.3). The bond valence model works for localized bonds between a cation and an anion which excludes most organic compounds but works very well for most inorganic compounds and also for hydrogen bonding. Compared to more precise electronical structural calculations, which would need to solve the Schrödinger equation, the BVS model is relatively simple and can be used in many different cases:

- Calculation of the oxidation state. Especially transition metals can have various stable oxidation states, which may change during the synthesis. BVS calculations can be used to assign the correct oxidation state or to guess relative amounts of different oxidation states in a mixed valence case. An example is the different oxidation states of copper in the superconductor YBCO.\[74]\n
- To validate new crystal structures. BVS values deviating from the expected ones could be due to wrong assignments of atoms or due to missing parts such as water molecules in the crystal structure.

- To distinguish between different atom types. In many structures the mixing of Si and Al is quite common and BVS calculations could be used to guess the relative amounts as it was done for e.g. CaAlSiN\[75].

- To introduce hydrogen atoms in the structure. Hydrogen is difficult to detect by single crystal diffraction and can therefore be added to oxygen with low valence values. An example is the synthetic mixite compound BiCu\textsubscript{6}(OH)\textsubscript{6}(AsO\textsubscript{4})\textsubscript{3}\cdot nH\textsubscript{2}O\[76]\ where the hydrogen positions have been determined based on BVS calculations and geometrical considerations.

Furthermore the BVS values can be used to decide if a cation anion interaction at a certain distance can be considered as bonded. According to Brown\[77]\ a covalent bond exists, if the valence exceeds 0.04 times the cation charge. For e.g. Cr\textsuperscript{3+} this means any bond with a bond valence contribution of at least 0.12 corresponding to a bond length of 2.54 Å for oxygen can be considered as bonded. This assumption has been used throughout this thesis and a table of maximum bond distances for selected cation anion pairs can be found in Table 1.1.
<table>
<thead>
<tr>
<th>Bond</th>
<th>$R_0$</th>
<th>$d_{\text{max}}$</th>
<th>$d_{\text{av}} (4)$</th>
<th>$d_{\text{av}} (6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$^{4+}$-O</td>
<td>1.811</td>
<td>2.75</td>
<td>2.07</td>
<td>2.22</td>
</tr>
<tr>
<td>Se$^{4+}$-Cl (Br)</td>
<td>2.22 (2.43)</td>
<td>3.15 (3.36)</td>
<td>2.48 (2.69)</td>
<td>2.63 (2.84)</td>
</tr>
<tr>
<td>Te$^{4+}$-O</td>
<td>1.977</td>
<td>2.91</td>
<td>2.23</td>
<td>2.38</td>
</tr>
<tr>
<td>Te$^{4+}$-Cl (Br)</td>
<td>2.37 (2.55)</td>
<td>3.30 (3.48)</td>
<td>2.63 (2.81)</td>
<td>2.78 (2.96)</td>
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<tr>
<td>Sb$^{3+}$-O</td>
<td>1.955</td>
<td>2.74</td>
<td>2.06</td>
<td>2.21</td>
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<tr>
<td>Sb$^{3+}$-Cl (Br)</td>
<td>2.35 (2.51)</td>
<td>3.13 (3.29)</td>
<td>2.46 (2.62)</td>
<td>2.61 (2.77)</td>
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<tr>
<td>V$^{5+}$-O</td>
<td>1.803</td>
<td>2.4</td>
<td>1.72</td>
<td>1.87</td>
</tr>
<tr>
<td>Cr$^{3+}$-O</td>
<td>1.724</td>
<td>2.51</td>
<td>1.83</td>
<td>1.98</td>
</tr>
<tr>
<td>Cr$^{3+}$-Cl (Br)</td>
<td>2.08 (2.28)</td>
<td>2.86 (3.06)</td>
<td>2.19 (2.39)</td>
<td>2.34 (2.54)</td>
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<td>1.790</td>
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<td>3.07 (3.27)</td>
<td>2.39 (2.60)</td>
<td>2.54 (2.75)</td>
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<td>2.67</td>
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<td>Fe$^{2+}$-Cl (Br)</td>
<td>2.06 (2.21)</td>
<td>2.99 (3.14)</td>
<td>2.32 (2.47)</td>
<td>2.47 (2.62)</td>
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<td>1.759</td>
<td>2.54</td>
<td>1.87</td>
<td>2.02</td>
</tr>
<tr>
<td>Fe$^{3+}$-Cl (Br)</td>
<td>2.09 (2.22)</td>
<td>2.87 (3.00)</td>
<td>2.20 (2.33)</td>
<td>2.35 (2.48)</td>
</tr>
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<td>Co$^{2+}$-O</td>
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<td>1.86</td>
<td>2.01</td>
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<td>Co$^{2+}$-Cl</td>
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<td>2.97</td>
<td>2.29</td>
<td>2.44</td>
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<tr>
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<td>1.675</td>
<td>2.61</td>
<td>1.93</td>
<td>2.08</td>
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<tr>
<td>Ni$^{2+}$-Cl</td>
<td>2.02 (2.20)</td>
<td>2.95 (3.13)</td>
<td>2.28 (2.46)</td>
<td>2.43 (2.61)</td>
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<tr>
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<td>1.679</td>
<td>2.61</td>
<td>1.94</td>
<td>2.09</td>
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<tr>
<td>Cu$^{2+}$-Cl (Br)</td>
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<td>2.93 (3.07)</td>
<td>2.26 (2.39)</td>
<td>2.41 (2.54)</td>
</tr>
<tr>
<td>Zn$^{2+}$-O</td>
<td>1.704</td>
<td>2.64</td>
<td>1.96</td>
<td>2.11</td>
</tr>
<tr>
<td>Zn$^{2+}$-Cl (Br)</td>
<td>2.01 (2.15)</td>
<td>2.94 (3.08)</td>
<td>2.27 (2.41)</td>
<td>2.42 (2.56)</td>
</tr>
</tbody>
</table>

Table 1.1  $R_0$ values, maximal bond distances and average bond lengths for 4 and 6 coordination of late transition metals in common oxidation states. All values are in Å.
1.5 Aim and Scope

This thesis describes the synthesis, crystal structure and physical properties of new transition metal oxides and oxo halides having lone-pair elements present in the crystal structure. Lone-pair elements are p-block elements having a stereochemically active lone-pair due to a np$^0$ns$^2$ electron configuration. Examples are e.g. Se$^{4+}$, Sb$^{3+}$, Te$^{4+}$, Bi$^{3+}$ or I$^{5+}$. Lone-pairs do not participate in chemical bonding but occupy non-bonded crystal volumes. Their one-sided asymmetric coordination make lone-pair elements therefore suitable structure directing entities, that are able to efficiently separate structure building blocks into lower dimensional arrangements. Other terminal ligands well known for opening up crystal structures are halide ions such as Cl$^-$, Br$^-$ or I$^-$. In the Lp-M-O-X system the combination of lone-pair elements and halide ions leads mainly to layered structural arrangements. The halide ions as well as the stereochemically active lone-pairs interact via ionic bonding or van der Waals interactions in between the layers and are responsible for the layer coherence along the stacking direction. The transition metals reside within the layers and form covalently bonded oxide/oxohalide nets together with the lone-pair elements. The separation of transition metal ions in well-defined layers has shown to result in interesting physical properties such as magnetic frustration, due to the arrangement of the metal ions within the metal oxide sheets. A low-dimensional arrangement of transition metal atoms may also exhibit other potentially interesting properties such as electrical or optical properties due to the high anisotropy found in these materials. To further separate the transition metal atoms and to find new interesting crystal structures within this class of compounds, the incorporation of well-defined tetrahedral building units, such as phosphates, sulphates, silicates and vanadates was investigated. To add an additional element into the structure increases the complexity form a synthesis point of view but allows to find new compounds having more complex arrangements and potentially interesting properties. Tetrahedral building blocks do not act as terminal ligands as halide ions and lone-pair elements but they have shown to be effective in separating structural entities by corner sharing and thus forming open framework structures. The goal of this thesis has been to further explore the concept of finding low-dimensional materials in the Trm-M-O-X system utilizing different transition metal cations. Compounds found in this system are known to be preferably layered with weak ionic or van der Waals interactions in between the layers. Furthermore, the incorporation of additional tetrahedral building blocks in this class of compounds has been investigated. Some of the new compounds have been characterized in terms of magnetic properties.
2. Experimental

2.1 Synthesis

Compounds presented in this thesis were obtained by either chemical reactions in evacuated silica tubes or by hydrothermal synthesis. The concept of finding new compounds is mainly based on trial and error by exploring different chemical systems using various molar ratios of the starting materials. Initial reaction conditions were obtained from experience of similar compounds previously synthesized. The process of finding new crystal phases is summarized in Figure 2.1.

**Figure 2.1** Flowchart describing the process of finding new compounds. Simple molar ratios are chosen for the synthesis that are later on improved according to EDS measurements to obtain suitable single crystals or even phase pure material.

The initial synthesis for finding new compounds is prepared from simple molar ratios of the starting materials at reaction temperatures, which worked well for similar materials. In this approach most reactions yielded a complex mixture, which may contain a novel phase mixed with unreacted starting material and/or additional side products. The molar ratio of the starting materials was then improved according to results obtained from *e.g.* EDS measurements to produce good quality single crystals. These crystals were isolated manually for the single crystal diffraction experiments under a light microscope to determine the crystal structure via single crystal X-ray diffraction. Knowing the exact composition, it was then possible to obtain phase
pure material for some few compounds for physical property measurements by further optimizing the synthesis conditions. The purity of the product was confirmed by powder diffraction prior to any measurements. Figure 2.1 shows crystals obtained from hydrothermal synthesis (a) CuSb$_6$O$_6$(SO$_4$)$_2$, (b) Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O) and from chemical reactions in silica tubes (c) Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$, (d) Fe$_3$Sb$_2$O$_4$Br$_2$ that are mounted on a glass pin.

Figure 2.1 Crystals obtained by hydrothermal synthesis: (a) CuSb$_6$O$_6$(SO$_4$)$_2$, (b) Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O) and by chemical reaction in silica tubes: (c) Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$, (d) Fe$_3$Sb$_2$O$_4$Br$_2$.

The synthesis of the new transition metal oxides and oxohalides was performed using transition metal oxides (MO), transition metal halides (MX) and lone-pair element oxides (LO) as starting materials as shown in Eq. 2.1 below. To introduce tetrahedral building units in the structure additional salts containing the tetrahedral units (TO) were used as starting materials, see Eq. 2.2. In this approach the halide ions could not always be included in the crystal structure, thus oxides were formed.

$$\text{MX} + \text{MO} + \text{LO} \rightarrow \text{M-L-O-X} \quad \text{(Eq. 2.1)}$$

$$\text{MX} + \text{MO} + \text{LO} + \text{TO} \rightarrow \text{M-L-O-TO}_4-(\text{Cl}) \quad \text{(Eq. 2.2)}$$

All chemicals used during synthesis were purchased from commercial suppliers and used without further purification. A list of the starting materials used and their purity is given in Table 2.1. All new compounds, the synthesis conditions and the molar ratios of starting materials are summarized in Table 2.2.
Table 2.1 Starting materials.

2.1.1 Chemical reactions in evacuated silica tubes

To avoid starting materials from evaporating and to maintain a closed reaction system, reactions were performed in evacuated silica tubes. For the sample preparation dry powders of the starting materials were weighted and ground thoroughly in an agate mortar before filling them into a silica tube. Samples containing (NH₄)H₂PO₄ were pre-heat-treated by putting the open tube with the starting materials into a muffle furnace for 1h at 250 °C to decompose the ammonium salt. The tube was then connected to a vacuum line to reduce the pressure inside the tube to about 10⁻² mbar. The silica tubes were then sealed under vacuum using a propane / oxygen gas burner. The reactions took place in a muffle furnace at a fixed temperature and reaction times from 1 day up to 1 month were used but normally 3 days turned out to be the optimal reaction time. All samples were allowed to furnace cool to room temperature before opening them. Silica tubes with diameter in between 6 mm - 12 mm and with a length of ca. 10-15 cm were used. Depend-
ing on the tube diameter total amounts of 0.5 g to 2 g of starting material was used for the sample preparation. A common problem with this synthesis method is the inclusion of unwanted water in the tubes, which can result in an explosion of the silica tube at higher temperature due to the pressure built up by the H₂O vapor. Some chemicals as e.g. FeCl₃ are very hygroscopic and a quick sample preparation is often needed in order to avoid severe water contamination.

The detailed mechanisms of the reactions are still somewhat unclear. During the reaction it’s likely that some kind of transport is involved as the reaction temperature is well below the melting points of the metal oxides and diffusion as known in traditional solid state reactions is unlikely. Most probably metal oxohalide intermediates like e.g. TeOCl₂ are involved to transport oxides with high melting points. To enhance the transport during reactions, different transport agents can be added. Typical transport agents are elemental iodine, HCl, or compounds that release halide gas at higher temperature. The single crystals often grow on top of the starting materials and can therefore more easily be separated from unreacted material.

2.1.2 Hydrothermal synthesis

Hydrothermal synthesis was carried out in Teflon lined steel autoclaves at temperatures up to 200°C. The volume of each autoclave is around 23 ml in which the starting materials were put with around 10 ml of deionized water. The amount of starting material used was in the order of 0.5 to 2 g. During an experiment the autoclave was heated at a fixed temperature for 3 to 7 days and furnace cooled afterwards before being opened. The crystals were filtered off, thoroughly washed with deionized water and allowed to dry in air. Due to the Teflon inlet of the autoclave the reaction temperature with this method is limited to about 220 °C. From experience compounds synthesized by the hydrothermal method are easier to obtain as pure phase in large amounts and the crystal size is often larger than observed with solid state reactions. An advantage is to avoid the use of transition metal oxides. Transition metal halides are mostly very soluble and easily removed as a byproduct through filtration. TeO₂ and Sb₂O₃ are very insoluble and crystals can often be cleaned from those oxides by using an ultrasonic bath. In most cases the outcome compared to reaction in evacuated silicon tubes at higher temperatures using the same starting materials will be very different except for few compounds as e.g. Cu₂Te₂O₅Cl₂[1] which seems to be a very stable phase and is even observed in reactions being far away from the stoichiometric ratio. It also seems to be more difficult to include halide ions into the structure using hydrothermal synthesis. One reason is the high solubility of the halide ions in water. On the other hand it is possible to include water molecules and hydroxyl groups into the structure which can lead to completely new phases not accessible with solid state reactions.
### Table 2.2

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Ratio</th>
<th>Starting materials</th>
<th>Final product</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C for 72 h</td>
<td>2:8:3:1</td>
<td>$\text{SO}_4^{2-} / \text{CuSO}_4$</td>
<td>IX</td>
<td></td>
</tr>
<tr>
<td>180°C for 48 h</td>
<td>2:2:1:1</td>
<td>$\text{Fe}_2\text{O}_3$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Co}_2\text{O}_3\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>180°C for 48 h</td>
<td>4:6:6</td>
<td>$\text{Fe}_2\text{O}_3$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Co}_2\text{O}_3\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>180°C for 48 h</td>
<td>4:1:1</td>
<td>$\text{Fe}_2\text{O}_3$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Co}_2\text{O}_3\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>180°C for 48 h</td>
<td>2:7:4:6:26</td>
<td>$\text{Te}_2\text{O}_3$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>I</td>
<td>(\text{Co}_2\text{Te}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
</tbody>
</table>

From hydrothermal synthesis:

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Conditions</th>
<th>Ratio</th>
<th>Starting materials</th>
<th>Final product</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>550°C for 70 h</td>
<td>1:2:1:1</td>
<td>$\text{SiO}_2$ / $\text{Na}_2\text{CO}_3$ / $\text{K}_2\text{CO}_3$</td>
<td>X</td>
<td>(\text{Na}_2\text{Si}_2\text{O}_5\text{PO}_4\text{Cl}_2)</td>
</tr>
<tr>
<td>2</td>
<td>570°C for 70 h</td>
<td>1:1:1:1</td>
<td>$\text{Te}_2\text{O}_3$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Co}_2\text{Te}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>3</td>
<td>570°C for 70 h</td>
<td>8:6:10</td>
<td>$\text{SiO}_2$ / $\text{Fe}_2\text{O}_3$ / FeCl$_3$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{Cl}_2)</td>
</tr>
<tr>
<td>4</td>
<td>570°C for 70 h</td>
<td>8:6:10</td>
<td>$\text{SiO}_2$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>5</td>
<td>570°C for 70 h</td>
<td>8:6:10</td>
<td>$\text{SiO}_2$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>6</td>
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<td>5:5:5</td>
<td>$\text{SiO}_2$ / $\text{Fe}_2\text{O}_3$ / FeCl$_3$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{Cl}_2)</td>
</tr>
<tr>
<td>7</td>
<td>50°C for 70 h</td>
<td>5:5:5</td>
<td>$\text{SiO}_2$ / FeCl$_3$ / FeCl$_2$ / FeCl$_4$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>8</td>
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<td>1:1:1</td>
<td>$\text{SiO}_2$ / $\text{Te}_2\text{O}_3$ / $\text{Fe}_2\text{O}_3$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{Cl}_2)</td>
</tr>
<tr>
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<td>50°C for 70 h</td>
<td>1:1:1</td>
<td>$\text{SiO}_2$ / $\text{Te}_2\text{O}_3$ / $\text{Fe}_2\text{O}_3$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
<tr>
<td>10</td>
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<td>1:1:1</td>
<td>$\text{SiO}_2$ / $\text{Te}_2\text{O}_3$ / $\text{Fe}_2\text{O}_3$</td>
<td>IA</td>
<td>(\text{Fe}_2\text{Si}_2\text{O}_5\text{PO}_4\text{(CH}_3\text{OH)}\text{H}_2\text{O})</td>
</tr>
</tbody>
</table>
2.2 Characterization

2.2.1 Single crystal X-ray diffraction (SXD)

Single crystal X-ray diffraction experiments were carried out on an Oxford Diffraction Xcalibur3 diffractometer equipped with a graphite monochromator. The single crystals were selected from the sample according to their size and morphology and glued onto a thin glass fiber using two-component glue for the measurement. The data collection was carried out at 293 K using MoKα radiation, λ = 0.71073 Å. Data reduction was done with the software CrysAlis RED that was also employed for the analytical absorption correction. The structure solution was carried out by SUPERFLIP implemented in Jana2006, SIR92 or SHELXS in the WINGX environment. The structural refinement was done in SHELXL or in Jana2006. The diffuse scattering found in the compound Co2Te3(PO4)O6Cl was simulated using the program DIFFaX and qualitively compared with observed diffraction patterns. The crystal structure of most oxo halides are rather straight forward and any of the above methods could be used for structure solution. Direct methods in the SIR software work very well if the correct formula is known. This information can be obtained by EDS analysis. Superfilp on the other hand is less sensitive to the chemical composition. Once an initial structural model was found using one of the structure solving methods above, missing atoms were assigned calculating the difference Fourier map. For standard refinements SHELXL has shown to be very effective and stable. It is the most used refinement method found in literature. For more complicated cases which involve twinning or structure modulation Jana2006 is more suitable. Jana was used to explain twinning in the structure Fe7(PO4)3Sb3O6X3 [Paper II]. All structures were refined by a full matrix least square refinement based on the structure factor F for Jana and based on the intensity (F^2) for SHELXL. The final R1 values were used as an indicator of how well the structural model fits the experimental data. Due to the different refinement modes this R values are expected to be lower Jana. The structural information from the refinement was saved as a Crystallographic information file (Cif) and was validated with the online checkCIF service, which uses the Platon software. The structural drawings were made using the program Diamond.

2.2.2 X-ray powder diffraction (PXRD)

Powder diffraction experiments were carried out on a PANalytical X’Pert pro diffractometer using Cu-Kα radiation. Data analysis was done with the software HighScore plus from PANalytical. For the measurement the sample
was dispersed on a zero background silicon wafer. Powder patterns were mainly collected to check the sample for phase purity, which is important for the physical measurements. To compare with experimental data powder diffractograms were calculated using the Mercury software.\cite{87} Comparison was done by manually comparing the peak positions without structural refinement.

2.2.3 Scanning electron microscopy (SEM)

To analyze the morphology and elemental composition of the sample a JEOL 7000F electron microscope equipped with an energy dispersive spectroscopy (EDS) detector was used. For the sample preparation crystals or powder sample were poured onto a sticky carbon foil glued onto the aluminum sample holder. Finally the sample was coated with a thin layer of carbon to make it conductive. This technique was mainly applied to determine the elemental composition of crystals and to compare with values found in the SXD experiment. SEM was also a useful tool to investigate crystals which were too small for SXD and so to improve the synthesis. Initial experiments done far apart from a stochiometric mixture of the starting materials often give only few very small crystals. Using the composition found by EDS gave useful information if the phase is new and how to perform the experiment.

2.2.4 Physical property measurement system (PPMS)

The magnetic susceptibility was measured with a physical property measurement system (PPMS) from Quantum Design equipped with a vibrating sample magnetometer (VSM). For the sample preparation small amounts of the sample was weighted and put into a plastic capsule, which was fixed onto a cylindrical copper holder. Magnetic measurements in papers I, III, V and X were done via collaboration on a MPMS SQUID magnetometer.

2.2.5 Thermogravimetry (TG)

The thermal decomposition and the release of crystal water were studied with a Perkin Elmer TGA7 thermo gravimetric analyzer with a heating rate of 10 °C / min in nitrogen atmosphere.

2.2.6 Infrared Spectroscopy (IR)

Infrared spectra were recorded on a Varian 670-IR FTIR spectrometer for the range 390–4000 cm\(^{-1}\) at ambient temperature. The spectrometer was equipped with an attenuated total reflection (ATR) detection device with a
single reflection ATR diamond element. IR was a useful tool to confirm crystal water in the structure.
3 Results and Discussion

A number of transition metal oxides and oxochlorides having lone-pair elements present have been synthesized and their crystal structures and some physical properties have been determined. Se$^{4+}$, Te$^{4+}$ and Sb$^{3+}$ were used as lone-pair elements and combined with various first row transition metals, PO$_4^{3-}$, SiO$_4^{4-}$, SO$_4^{2-}$ and VO$_4^{3-}$ as tetrahedral building blocks and Cl$^-$ or Br$^-$ as halide ions. The results are presented in two parts:

(1) In the Trm-Lp-O-X (Trm = transition metal, Lp = lone-pair element, X = halide) system the compounds have crystal structures that are predominantly layered with the halide ions and the lone-pairs occupying non-bonded space at the layer interface. Individual layers stick together by weak van der Waals interactions or ionic bonding, whereas transition metal oxides are well isolated in the middle of the layers.

(2) The inclusion of tetrahedral building blocks into transition metal oxides and oxohalides having a lone-pair element present was investigated and new compounds containing phosphate (PO$_4$), silicate (SiO$_4$), sulphate (SO$_4$) and vanadate (VO$_4$) groups are presented. Those additional tetrahedral building blocks lead to new interesting crystal structures such as the formation of unusual solid solutions or to hydrogen bonding due to the inclusion of hydroxyl groups.

The new compounds were characterized by single crystal X-ray diffraction and whenever possible, physical properties (mainly magnetic properties) were also measured. A detailed description of the synthesis, crystal structure and physical properties of the different compounds can be found in the corresponding papers (I-X). Space groups and unit cells of the new compounds are summarized in Table 3.1.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Paper</th>
<th>Space group</th>
<th>(a, (\text{Å}))</th>
<th>(b, (\text{Å}))</th>
<th>(c, (\text{Å}))</th>
<th>(\alpha, (^\circ))</th>
<th>(\beta, (^\circ))</th>
<th>(\gamma, (^\circ))</th>
</tr>
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<tbody>
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<td>III</td>
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<td>17.3394(2)</td>
<td>17.5405(2)</td>
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<td>90</td>
<td>90</td>
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<tr>
<td>(\text{Mn}_2\text{Te}<em>2\text{O}</em>{12}\text{Cl}_2) *</td>
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<td>(P2_1/c)</td>
<td>8.6904(2)</td>
<td>5.4808(1)</td>
<td>16.144(5)</td>
<td>90</td>
<td>107.570(3)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{MnSb}_2\text{O}_3\text{Cl}_2) *</td>
<td>VII</td>
<td>(P2_12_12_1)</td>
<td>5.4698(2)</td>
<td>5.5479(2)</td>
<td>31.0882(9)</td>
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<td>90</td>
<td>90</td>
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<tr>
<td>(\text{Mn}_2\text{Sb}_2\text{O}_4\text{Cl}) *</td>
<td>VII</td>
<td>(P2_1/c)</td>
<td>7.2406(6)</td>
<td>9.8413(7)</td>
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<td>90</td>
<td>104.596(9)</td>
<td>90</td>
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<td>(\text{Mn}_2\text{Sb}_2\text{O}<em>4\text{Cl}</em>{10}) *</td>
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<td>(P2_1)</td>
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<td>90</td>
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<td>(Cmca)</td>
<td>6.3099(1)</td>
<td>12.3959(3)</td>
<td>14.5287(3)</td>
<td>90</td>
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<tr>
<td>(\text{Fe}_2\text{Sb}_2\text{O}<em>4\text{Cl}</em>{10}) *</td>
<td>VII</td>
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<td>(\text{Co}_2\text{Te}_3\text{O}_4\text{Cl}_2\text{H}<em>2\text{O})</em>**</td>
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<td>(P2_1/m)</td>
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<td>90</td>
<td>94.159(1)</td>
<td>90</td>
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<td>(\text{Mn}_2\text{Te}_2\text{O}_4\text{Cl}_2\text{H}_2\text{O}) *</td>
<td>V</td>
<td>(P2_1/m)</td>
<td>5.5463(3)</td>
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<td>(\text{Co}_2\text{Te}_2\text{O}_4\text{Cl}_2\text{H}_2\text{O}) *</td>
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<td>(P2_1/c)</td>
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<td>38.088(5)</td>
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<td>94.875(8)</td>
<td>90</td>
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<tr>
<td>(\text{Fe}_2\text{PO}_4\text{Sb}_2\text{O}_4\text{Cl}) *</td>
<td>II</td>
<td>(Pnma)</td>
<td>5.1852(1)</td>
<td>14.8848(4)</td>
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<td>90</td>
<td>90</td>
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<tr>
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<td>(Pnma)</td>
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<td>25.935(3)</td>
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<td>90</td>
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<tr>
<td>(\text{Fe}_2\text{Te}_2\text{O}_4\text{Cl}_2\text{H}_2\text{O}) *</td>
<td>VIII</td>
<td>(C2/c)</td>
<td>20.5816(5)</td>
<td>26.7506(6)</td>
<td>5.0391(1)</td>
<td>90</td>
<td>93.587(2)</td>
<td>90</td>
</tr>
<tr>
<td>(\text{Co}_2\text{Se}_2\text{O}_4\text{Cl}_2\text{H}<em>2\text{O})</em>**</td>
<td>IV</td>
<td>(P, -1)</td>
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<td>8.0377(3)</td>
<td>8.8398(4)</td>
<td>66.029(4)</td>
<td>68.616(4)</td>
<td>69.286(3)</td>
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<tr>
<td>(\text{Co}_2\text{Se}_2\text{O}_4\text{Cl}_2\text{H}<em>2\text{O})</em>**</td>
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<td>(P, -1)</td>
<td>7.8766(3)</td>
<td>8.0351(3)</td>
<td>8.8494(3)</td>
<td>66.147(4)</td>
<td>69.313(4)</td>
<td>69.313(4)</td>
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<tr>
<td>(\text{Co}_2\text{Se}_2\text{O}_4\text{Cl}_2\text{H}<em>2\text{O})</em>**</td>
<td>IV</td>
<td>(P, -1)</td>
<td>7.8843(4)</td>
<td>8.0391(4)</td>
<td>8.8404(4)</td>
<td>66.099(6)</td>
<td>68.666(6)</td>
<td>69.339(6)</td>
</tr>
<tr>
<td>(\text{CuSb}_2\text{SO}_4\text{O}_8) **</td>
<td>IX</td>
<td>(P, -1)</td>
<td>5.5404(2)</td>
<td>7.6891(4)</td>
<td>9.2358(4)</td>
<td>96.560(3)</td>
<td>93.780(4)</td>
<td>109.740(3)</td>
</tr>
<tr>
<td>(\text{Mn}_2\text{Sb}_2\text{V}_2\text{O}_4\text{O}_3\text{Cl}_3) **</td>
<td>X</td>
<td>(P, -1)</td>
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<td>7.9133(4)</td>
<td>8.3505(3)</td>
<td>72.266(4)</td>
<td>74.336(4)</td>
<td>72.018(5)</td>
</tr>
</tbody>
</table>

**Table 3.1**: Summary of the new compounds discussed in this thesis. *from reactions in sealed silica tubes, **from hydrothermal synthesis.
3.1 Layered Trm-Lp-O-X compounds

Investigations in the Trm-Lp-O-X (Trm = Cr$^{3+}$, Mn$^{2+}$, Fe$^{3+}$, Lp = Te$^{4+}$, Sb$^{3+}$, X = Cl, Br) system lead to the discovery of nine new compounds described in detail in papers III and VII. The compounds found in this system are very similar in terms of their topology. The crystal structures are layered, and the halide ions and stereochemically active lone-pairs were found to reside in non-bonding volumes in between the layers while the transition metal oxide building blocks are situated within the layers. We can differentiate between two different types of layer arrangements as shown in Figure 3.1: (i) the halide ions and lone-pairs protrude from charge neutral layers that hold together by weak van der Waals interactions and (ii) the lone-pairs protrude from positively charged layers that are held together by ionic bonding through the halide ions located in between the layers.

![Figure 3.1](image)

**Figure 3.1** Stacking of charge neutral layers through weak van der Waals interactions in Mn$_5$Te$_5$O$_{12}$Cl$_2$ and stacking of layers held together by ionic bonding in Cr$_5$Te$_5$O$_{13}$Cl$_3$.

Structures having a layered arrangement within the Trm-Lp-O-X system are obtained due to the combination of lone-pair cations and halide ions. The terminating species, namely the halide ions and lone-pair elements, separate the transition metal oxide/oxohalide building blocks by forming a non-bonded volume in between the layers. With the presence of oxygen atoms, covalent bonding between lone-pair elements and halide ions is unlikely because the lone-pair ions are hard Lewis acids due to their relatively high charge and small ionic radius that prefer to bond to hard Lewis base oxygen atoms according to the hard-soft acid-base concept. Transition metals with the intermediate charge (2+) are softer and frequently bond to both oxygen and halide ions. This concept holds well for structures with relatively soft cations such as Mn$^{2+}$, which preferably form charge neutral layers that are held together by van der Waals interactions. An exception among the struc-
atures found in this work is the compound MnSb₄O₆Cl₂, where positively charged layers are linked through ionic bonding. This might be due to the low Mn/Sb ratio in this particular structure. The layer framework is mainly made up by the antimony oxide building blocks in which the outnumbered isolated manganese polyhedra are located. This arrangement does not allow the halide ions to protrude from the layers. Such types of layer stacking is more common with strong Lewis acid transition metal cations such as Cr³⁺, which prefer to bond towards oxygen, so that the halide atoms are forced to coordinate towards the lone-pair cations in between positively charged layers as observed in Cr₃Te₅O₁₃Cl₃ [Paper III]. Both ionic bonding and van der Waals interactions in between the layers are much weaker than the covalent bonding interaction within the layers, which leads to single crystals having a plate-like morphology due to slow crystal growth in the direction perpendicular to the layers.

It is not possible to predict in advance which compounds are stable and which synthesis conditions are best. For example, for Cr³⁺ a compound could be found containing Te⁴⁺, but attempts with Sb³⁺ failed despite testing different ratios of starting material over a wide range of reaction temperatures. For Mn²⁺, however, many different compounds seem to exist with Te⁴⁺ as well as Sb³⁺ by changing the stoichiometry and reaction conditions. One reason for this could be that this transition metal ion is more flexible in terms of coordination. While most first row transition metals prefer octahedral coordination, the absence of the ligand field stabilization energy due to the d⁵ electron configuration of Mn²⁺ can result in very distorted coordination polyhedra as shown in Figure 3.2.

![Figure 3.2](image)

Figure 3.2 Different coordination polyhedra for Mn²⁺. Distorted [MnO₂Cl₂] tetrahedra, [MnO₃Cl₂] square pyramid, [MnO₂Cl₄] octahedra and [Mn₄Cl₃] pentagonal bipyramid.

The coordinations of the lone-pair elements Te⁴⁺ and Sb³⁺ are quite similar. Both cations have a very asymmetric one-sided coordination due to the stereochemically active lone-pair and preferably form either [LpO₃] trigonal pyramids or [LpO₄] see-saws. Despite their similarities in coordination, completely different crystal structures are usually obtained using either Te⁴⁺ or Sb³⁺ due to their difference in charge. For the series of isostructural compounds M₇Sb₁₀O₁₈X₈ (M = Fe,Mn; X = Cl,Br) it was possible to replace Cl
with Br and Mn with Fe without changing the structure. It is common that Cl can be replaced by Br in these kinds of layered compounds and most often only small changes, such as variation of the interlayer distance due to the different size of the anions, occur in the crystal structure. The exchange of transition metals within the same structure, however, is of more importance because it can be used to completely change the physical properties of the material such as for example the magnetic properties. Among layered transition metal oxohalides there are only a few examples where the transition metal can be exchanged without changing the crystal structure. It is mostly a replacement of Ni$^{2+}$ with Co$^{2+}$ as in M$_5$(SeO$_3$)$_4$X$_2$ (M=Co,Ni; X=Cl,Br)\cite{88} or (Co$_{1-x}$)$_3$Sb$_4$O$_6$F$_6$.\cite{89} The synthesis concept of using lone-pair elements in combination with halide ions has shown to be successful with other transition metals such as Co, Ni, Cu or Zn. Some examples are Co$_5$Te$_3$O$_{12}$Cl$_2$,\cite{7} Ni$_3$Te$_3$O$_{12}$Cl$_2$,\cite{90} Cu$_2$Te$_2$O$_3$Cl$_2$\cite{91} or Zn$_2$Te$_2$O$_3$Cl$_2$.\cite{91} Although most of the compounds found in this system are layered, other interesting structural arrangements have also been observed such as for example clusters in Cu$_{20}$Sb$_{35}$O$_{44}$Cl$_{37}$,\cite{92} columns in [Sb$_4$O$_{7+3\delta}$X$_4$][Zn$_3$]$_{1+\delta}$ (X = Cl,Br,I)\cite{93} and small channels in the open framework structure Fe$_6$Ca$_2$(SeO$_3$)$_9$Cl$_4$.\cite{94}

### 3.2 Structures with tetrahedral building blocks

It was possible to incorporate tetrahedral building blocks (PO$_4$, SiO$_4$, SO$_4$, VO$_4$) into transition metal oxides and oxohalides having a lone-pair element by using either hydrothermal synthesis or chemical reactions in evacuated silica tubes at a high temperature. In the hydrothermal approach only oxides were obtained, while with gas phase solid reactions it was also possible to include halide ions into the crystal structure. Neither of the tetrahedral groups found in the structures described below polymerize, but they separate other building blocks by corner sharing.

#### 3.2.1 Tubular units in Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$X$_3$ (X=Cl, Br)

The compound Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$X$_3$ (X=Cl, Br) is built from tubular Fe$_7$(PO$_4$)$_3$O$_6$X$_3$ units that extend along [100]. Each tube is further connected to six tubular units in the (100) plane by the antimony oxide building blocks that act as linkers, as shown in Figure 3.3. Each tube is constructed from an outer shell of edge sharing iron oxide octahedra, which is separated by phosphate groups to a linear chain of face sharing [FeO$_6$] octahedra in the center. The face sharing leads to remarkably short Fe-Fe distances in the central chain of ~2.56 Å. Connecting only the iron atoms of the outer shell of a tube reveals an arrangement similar to a carbon nano tube (see insert in Figure 3.3).
Although the individual tubes have perfect $P6_3mm$ symmetry the crystal system is found to be orthorhombic due to the arrangement of the tubes in the crystal structure. The similar orientation of the phosphate groups within the tubular units results in a dipole moment. The resulting charge separation is compensated by neighboring tubes having a reversed orientation, which breaks the hexagonal symmetry (see Figure 3.4). In fact, the crystal is constructed by the regular alternation of layers having the same and opposite orientations of the tubes. Looking at the arrangement of the transition metals within the structure, the compound can be regarded as being one-dimensional, and due to the short Fe-Fe distances the material may exhibit interesting electrical properties. However, the crystals obtained were unfortunately too small for any resistivity measurement.

The crystal structure of Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$X$_3$ is closely related to the one found in the mineral holtite $Ta_{0.6}Al_{6}B_{3}Si_{3}O_{18}$,\textsuperscript{95} dumortierite (Al)$_6$BSi$_3$O$_{18}$\textsuperscript{96} or szklaryite Al$_6$BAs$_3$O$_{15}$\textsuperscript{97} The mineral structures are built from similar tubular units that have linear chains of face sharing octahedra in the center. Instead of iron oxohalide the framework is mainly built from aluminum oxide building blocks.
The net dipole moment found in each tubular unit caused by a unidirectional arrangement of the phosphate groups is compensated through reversing the orientation of neighboring tubes.

3.2.2 Layered $\text{Co}_2\text{Te}_3(\text{PO}_4)\text{O}_6\text{Cl}$, $\text{CuSbO}_8(\text{SO}_4)_2$ and $\text{Mn}_4(\text{TeO}_3)(\text{SiO}_4)\text{X}_2$ ($\text{X}=\text{Br,Cl}$)

The compounds $\text{Co}_2\text{Te}_3(\text{PO}_4)\text{O}_6\text{Cl}$ and $\text{Mn}_4(\text{TeO}_3)(\text{SiO}_4)\text{X}_2$ ($\text{X}=\text{Br,Cl}$) were both synthesized via chemical reactions in evacuated silica tubes, while $\text{CuSbO}_8(\text{SO}_4)_2$ was obtained from hydrothermal synthesis. All three crystal structures are built from charge neutral layers that are held together by weak van der Waals interactions. The transition metal atoms are located in the middle of the layers bound to the tellurium/antimony oxide building blocks and take different kinds of arrangements. The halide ions as well as lone-pairs protrude from the layers (see Figure 3.5). In $\text{Co}_2\text{Te}_3(\text{PO}_4)\text{O}_6\text{Cl}$ the transition metal atoms are arranged in zigzag chains of edge sharing cobalt oxide and oxohalide octahedra. The chains are separated from each other by phosphate and tellurium oxide building blocks. The layer coherence is given by weak van der Waals interactions between the tellurium and oxygen atoms at the layer interface. Relatively large channels are observed in between the layers compared to other related layered compounds, which results in the formation of stacking faults, discussed in more details in chapter 3.5. In $\text{Mn}_4(\text{TeO}_3)(\text{SiO}_4)\text{X}_2$, the manganese atoms are arranged in extending oxohalide nets. There are two nets per layer, which are separated by each other through silicate groups. In this case the layers are held together through interactions involving both the lone-pairs and the halide ions. In the compound $\text{CuSbO}_8(\text{SO}_4)_2$ the copper polyhedra are isolated through the antimony oxide network. In this case no halide ions are present in the structure and the layer coherence is realized by van der Waals interactions between lone-pair elements and sulphate groups protruding from the layers.
3.2.3 Open framework structures

In total, four new open framework compounds were found having a transition metal, a lone-pair element and tetrahedral building blocks in the structure. The two oxides \( \text{Co}_3\text{Te}_2\text{O}_2(\text{PO}_4)_2(\text{OH})_4 \) and \( \text{Co}_3(\text{SeO}_3)_3(\text{PO}_3\text{OH})_x(\text{H}_2\text{O}) \) (Figure 3.6) were obtained from hydrothermal methods, while the two oxohalide compounds \( \text{Fe}_{11}\text{Te}_5(\text{PO}_4)_2\text{O}_{22}\text{Cl}_3 \) and \( \text{Mn}_3\text{Sb}_{2.1}(\text{VO}_4)_{1.9}\text{O}_{2.3}\text{Cl}_2 \) (Figure 3.7) could be synthesized via chemical reactions in evacuated silica tubes. Although the lone-pair elements are not able to effectively reduce the dimensionality by e.g. formation of layers as described in chapter 3.2.2, the stereoactive lone-pairs from the p-elements still protrude into non-bonding volumes in the crystal structures, leading to the formation of small channels. Furthermore, the presence of corner sharing coordination polyhedra allows separation of the transition metal polyhedra into different arrangements.

In the compound \( \text{Co}_3\text{Te}_2\text{O}_2(\text{PO}_4)_2(\text{OH})_4 \) the cobalt oxide polyhedra are arranged in linear chains or isolated \( [\text{CoO}_6] \) octahedra. Neither the tellurium oxide nor the phosphate building blocks polymerize. In the solid solution \( \text{Co}_3(\text{SeO}_3)_3-x(\text{PO}_3\text{OH})_x(\text{H}_2\text{O}) \) the cobalt oxide polyhedra construct a complex framework having small channels in which the selenium oxide and phosphate groups reside. Both the oxide structures have hydroxyl ions or crystal water present in the structure, which participate in strong hydrogen bonding. A rather complex arrangement of the iron oxohalide building blocks into layers, which are separated by tellurium oxide entities, is observed in the compound \( \text{Fe}_{11}\text{Te}_5(\text{PO}_4)_2\text{O}_{22}\text{Cl}_3 \). The lone-pairs as well as the halide ions protrude into small cavities. The rather low concentration of

\[ \text{Figure 3.5 Overview of the layered structures } \text{Co}_2\text{Te}_3(\text{PO}_4)_6\text{Cl}, \text{CuSbO}_6(\text{SO}_4)_2 \text{and } \text{Mn}_4(\text{TeO}_3)(\text{SiO}_4)X_2. \]
phosphate groups in the structure do not allow the transition metal building blocks to separate.

![Figure 3.6](image1.png) Overview of the framework structures Co₃Te₂O₂(PO₄)₂(OH)₄ and Co₃(SeO₃)₃₋ₓ(PO₃OH)ₓ(H₂O). Hydrogen bonds are drawn as dotted lines.

In Mn₃Sb₂₋₁(VO₄)₁₋ₓO₂₋ₓClₓ, the manganese oxochloride building blocks are arranged into linear chains of edge sharing polyhedra, which are well separated from each other through the vanadium oxide and antimony oxide building blocks. Again, the lone-pairs as well as the halide ions protrude into small channels.

![Figure 3.7](image2.png) Overview of the oxohalide structures Fe₁₁Te₅(PO₄)₂O₂Cl₃ and Mn₃Sb₂₋₁(VO₄)₁₋ₓO₂₋ₓClₓ.
3.3 Solid solutions: Split positions involving a lone-pair element

A solid solution is formed when two or more different types of atoms can be exchanged in a compound without changing its crystal structure. Elements that can form a solid solution are mostly close neighbors in the periodic table as an exchange in the crystal structure is often only possible for atoms having similar size, charge and coordination. Experiments showed that lone-pair atoms are able to form rather uncommon solid solutions and the split positions of \( \text{Se}^{4+}/\text{P}^{5+} \) and \( \text{Sb}^{3+}/\text{V}^{5+} \) in the two compounds \( \text{Co}_3(\text{SeO}_3)_{3-x}(\text{PO}_3\text{OH})_x(\text{H}_2\text{O}) \) \((0.78<x<1.16)\) and \( \text{Mn}_3\text{Sb}_{2+x}(\text{VO}_4)_{2-x}\text{O}_{2+3x}\text{Cl}_2 \) \((0.08<x<0.13)\) are discussed. \( \text{Se}^{4+} \) and \( \text{P}^{5+} \) differ in charge, size and coordination behavior. \( \text{P}^{5+} \) coordinated by oxygen forms regular tetrahedra while \( \text{Se}^{4+} \) adopts an asymmetric trigonal pyramidal coordination including also the stereochemically active lone-pair. With a bond distance of around 1.54 Å, the P-O bond is significantly smaller than the average Se-O bond of ~1.7 Å. It is therefore obvious that the selenium and phosphorus atoms cannot be at exactly the same position within the crystal structure if the two replace each other but form a split position with the Se atoms being further apart from the bonded oxygen atoms as shown in Figure 3.8.

![Figure 3.8 Split position of Se^{4+} and P^{5+}](image)

The exchange of Se and P within the compound \( \text{Co}_3(\text{SeO}_3)_{3-x}(\text{PO}_3\text{OH})_x(\text{H}_2\text{O}) \) is possible only because the split position is located on the surface of small pore walls. Replacing building blocks with a different size may influence the size and/or the chemical properties of the pores but will not affect the crystal structure itself, as the building blocks have space to expand towards the inside of the pore. Depending on whether it is Se or P that occupies the split
position either the lone-pair or the hydroxyl group is protruding into the pores. Se\(^{4+}\) and P\(^{5+}\) are different in charge but the overall charge is balanced looking at the complete building blocks \([\text{SeO}_3]^{2-}\) and \([\text{PO}_3\text{OH}]^{2-}\), which are exchanged. In the current example, two different sites for possible split positions are observed, and depending on how much phosphate is added as starting material, different Se/P occupations are observed. With a low phosphate content only the first split position is partially occupied by about 80 % P and 20 % Se. By increasing the phosphor content a second split position is also formed, and increasing the phosphate concentration even more results in fully occupying the first split position by phosphorous and increased phosphor content in the second split position (see Table in Figure 3.8).

A similar situation is present in Mn\(_3\)Sb\(_{2+x}\)(VO\(_4\))\(_{2-3x}\)O\(_{2.55}\)Cl\(_2\) where a split position between Sb\(^{3+}\) and V\(^{5+}\) is found. Vanadium adopts a distorted tetrahedral VO\(_4\) coordination with average bond lengths of around 1.7 Å. Antimony, on the other hand, has a trigonal pyramidal coordination with the stereochemically active lone-pair present. Average Sb-O bond distances are around ~1.9 Å and substantially longer than observed for V-O bonds, which results in a clear separation of the two atom positions. Taking into account the net charge of the entire building blocks \([\text{VO}_4]^{3-}\) and \([\text{SbO}_3]^{3-}\), the overall charge balance in the structure is not affected. Other than in Co\(_3\)(SeO\(_3\))\(_{3.1-3x}\)(PO\(_3\text{OH}\))\(_x\)(H\(_2\)O), the split position is not located towards a pore but directly in the structure framework, and a Sb/V exchange will therefore also affect the coordination of the manganese atom Mn\(_2\). When vanadium is occupying the split position Mn\(_2\) adopts octahedral [MnO\(_4\)Cl\(_2\)] coordination, and with the presence of antimony the coordination changes to square planar [MnO\(_2\)Cl\(_2\)]. This might be the reason for the relatively narrow range of the solid solution, as with a higher amount of Sb\(^{3+}\), and therefore more [MnO\(_2\)Cl\(_2\)] polyhedra the structure may become unstable. The compound could only be synthesized with a molar ratio of the starting materials relatively close to the theoretical one, and a significant amount of an impurity oxide phase was always present, which is in fact very similar in terms of crystal morphology and color. Synthesis attempts with variable V and Sb contents were not successful, and the range of the solid solution given here is based on the structure refinement of three different crystals from the same batch. These kinds of solid solutions found in Co\(_3\)(SeO\(_3\))\(_{3.1-3x}\)(PO\(_3\text{OH}\))\(_x\)(H\(_2\)O) and Mn\(_3\)Sb\(_{2+x}\)(VO\(_4\))\(_{2-3x}\)O\(_{2.55}\)Cl\(_2\) are relatively rare, but a similar split position of Sb and V is found for example in the defect pyrochlore (Na\(^{+1.08}\)V\(^{5+}_{0.43}\)Sb\(^{3+}_{0.14}\))(Sb\(^{5+}\)O\(_6\))O\(_{0.84}\)\(^{[98]}\) where a shared position between Na, Sb and V is observed. In the mineral Holtite (Si\(_{2.25}\)Sb\(_{0.75}\))B[Al\(_8\)(Al\(_{0.43}\)Ta\(_{0.27}\))O\(_{15}\)(O,OH)\(_{2.25}\)]\(^{[95]}\) a split position between Si\(^{4+}\) and Te\(^{4+}\) can be seen. In this case the split position is located within the framework and is accompanied with a replacement of Al through Ta to obtain charge balance. From these two compounds a structure description is based on only one crystal and no information about the range of the solid
solution is given. More common are solid solutions where a lone-pair cation is replaced by another one with the same oxidation state. An example is the compound (Sb,Bi)$_2$S$_3$ where the solid solution is stable over a wide range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V1 / Sb2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0.94 / 0.06</td>
</tr>
<tr>
<td>2b</td>
<td>0.95 / 0.05</td>
</tr>
<tr>
<td>2c</td>
<td>0.96 / 0.04</td>
</tr>
</tbody>
</table>

Figure 3.9  Split positions of Sb$^{3+}$ and V$^{5+}$ in compound Mn$_3$Sb$_{2+x}$(VO)$_{4-3x}$O$_{2+3x}$Cl$_2$.

### 3.4 Hydrogen bonding

Hydrothermal synthesis has shown to be a great complementary technique for finding new compounds, which are otherwise not accessible using chemical reactions at high temperatures. Compounds found by hydrothermal synthesis often include crystal water or hydroxyl groups in the crystal structure as observed for Co$_3$Te$_2$O$_2$(PO$_4$)$_2$(OH)$_4$ and Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O). In most cases it is not possible to locate the hydrogen atoms directly from the difference Fourier map of the X-ray diffraction experiment due to the combination of the light weight of the hydrogen atom and the more heavy atoms present in the structure. Therefore, hydrogen atoms are inserted by means of geometrical considerations and with the aid from bond valence sum calculations. To confirm the presence of hydrogen in the structure in the form of hydroxyl groups or water molecules, IR measurements can be performed, which show characteristic bands in the high energy region of the spectra. However, no information about the quantity or atomic position can be obtained from this method. The total amount of hydrogen atoms in the structure can be calculated by charge balancing the sum formula. Information regarding to which oxygen atoms the hydrogens are bonded can often be obtained looking at the BVS values. Oxygen to which the hydrogen atoms are connected are expected to have a significantly lower BVS value than 2. If there
is strong hydrogen bonding present in the structure the oxygen accepting the hydrogen bond is also supposed to have a slightly lower BVS value.

Figure 3.10 Hydrogen bonding distances in (a) Co$_3$Te$_2$O$_2$(PO$_4$)$_2$(OH)$_4$ and (b-c) Co$_3$(SeO$_3$)$_3$$_x$(PO$_3$OH)$_x$(H$_2$O).

For Co$_3$Te$_2$O$_2$(PO$_4$)$_2$(OH)$_4$, a hydroxyl group could be identified on O(5), which has a BVS value of 1.19. An O-H bond distance of 0.95 Å was calculated from the BVS data to increase the BVS value of O(5) to exactly 2. The hydrogen bond accepting oxygen atom is O(4), that has a somewhat lower BVS value of 1.6. The hydrogen atom was placed in between these two oxygen atoms resulting in a hydrogen bond length of ~1.9 Å. The compound Co$_3$(SeO$_3$)$_3$$_x$(PO$_3$OH)$_x$(H$_2$O) has both a hydroxyl group and crystal water present. With a BVS value of only 0.3, O(7) was assigned to belong to the H$_2$O molecule, while O(5) (BVS 1.6) needs to be a hydroxyl ion. In this case the O-H bond length was not refined using BVS data but directly fixed to 0.8 Å. For the hydroxy group this results in a hydrogen bonding distance of around 1.73 Å towards O(6) (BVS 1.6). For the H$_2$O molecule the O-H bond lengths were fixed to 0.8 Å, and the H-O-H angle was restrained close to 104°. The water molecule was then oriented so that it could form hydrogen bonds to surrounding oxygen atoms, which results in hydrogen bonding distances of around 1.9 Å and 2.3 Å towards O9 and O2, respectively. Similar oxide compounds having crystal water or hydroxyl ions present are for example NaCo$_3$(PO$_4$)(HPO$_4$)$_2$,$^{[100]}$ (NH$_4$)$_4$[V$_2$O$_7$(OH)$_2$]·2H$_2$O$^{[101]}$ and NH$_4$RbTe$_4$O$_9$·2H$_2$O.$^{[102]}$ The positions of the hydrogen atoms within the crystal structure that were determined using the approach of simple geometrical considerations, and BVS values may not be very accurate, but they are sufficient to understand the structural model and the ongoing hydrogen
bonding. A more accurate description might be obtained from neutron diffraction experiments as has been done for Te(OH)$_6$·2Na$_3$P$_3$O$_9$·6H$_2$O.$^{[103]}$

### 3.5 Diffuse scattering due to faulted stacking of layers

Diffuse scattering was observed in the compound Co$_2$Te$_3$(PO$_4$)O$_6$Cl [Paper VI]. Looking at the diffraction pattern of e.g. the (100) plane one can observe sharp diffraction peaks along lines with $k = 2n$ but diffuse streaks for lines having $k = 2n+1$. Periodic order of atoms within a crystal will lead to diffraction patterns having sharp Bragg peaks, which are well separated from each other depending on the size of the smallest repeating unit, the unit cell. Additional diffraction intensities such as diffuse blobs or streaks indicate a break in periodicity caused by disorder within the crystal. Diffuse streaks affecting only certain diffraction lines along a specific crystallographic direction are a strong indication of the presence of stacking faults. Up to now there is no standard way of analyzing structures showing diffuse scattering, and investigations are often based on the qualitative comparison of calculated and observed diffraction patterns. In the current example layers of cobalt tellurium oxo phosphate chloride stack along [001] and are connected only through weak van der Waals interactions. The diffuse lines make the choice of the correct unit cell and the structure solution difficult. The structure could be refined in either a triclinic unit cell with the space group $P-1$, where the layers are related by a shift to each other, or in a larger monoclinic cell with space group $P2_1/c$ where the layers stack according to a glide operation. From this observation one can conclude, that the stacking arrangement in the true crystal must be a combination of a glide and shift operation.

![Figure 3.11](image) The charge neutral layers of Co$_2$Te$_3$(PO$_4$)O$_6$Cl randomly stack by either a glide or shift operation within the crystal.
To prove this assumption a simulation was performed using the program DIFFaX. The layers were allowed to randomly stack by either a layer shift or a glide operation. The two stacking possibilities and an example stacking sequence are shown in Figure 3.11. The outcome of the simulation is shown in Figure 3.12 in comparison with the experimental diffraction pattern of the h1l layer. As previously discussed, a layered arrangement within transition metal oxochlorides having a lone-pair element present is very common. The layer interactions are mainly given through weak van der Waals interactions between the lone-pairs and the halide ions. It is therefore surprising that this kind of irregular layer stacking was not observed for similar crystal structures. The main reason for this could be the relatively large pores found in between the layers, weakening the van der Waals interactions and also creating two nearly equal relations in between the layers. These two layer transitions occur randomly within the crystal. It is quite common to have two symmetry related layers per unit cell as in e.g. $\text{Co}_5(\text{TeO}_3)_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$)\textsuperscript{104} or $\text{Cd}_7\text{Cl}_8(\text{Te}_7\text{O}_{17})$\textsuperscript{105} but in this case the ABAB stacking is regular throughout the crystal. Diffuse scattering is widely occurring in simple structures adopting basic crystal packing as in e.g. $\text{SiC}$\textsuperscript{106} or $\text{GaN}$\textsuperscript{107} Stacking faults are also very common among minerals such as in e.g. layered brownmillerites.\textsuperscript{108}

Figure 3.12  Reconstructed diffraction image of the h1l plane (left) compared to the calculated one using DIFFaX.

### 3.6 Magnetic measurements

Some of the new structures found during this work were characterized in terms of magnetic properties. Table 3.2 summarizes the results of the magnetic investigation of the different compounds. As those measurements are
rather sensitive to magnetic impurities, the powders were first checked for secondary impurity phases under the light microscope and by powder X-ray diffraction. To characterize the magnetic properties of the compounds three methods were mainly used:

- Magnetic susceptibility versus temperature at constant magnetic fields using either field cooled (FC) or zero field cooled (ZFC) conditions.
- Magnetization versus magnetic field at constant temperature.
- Heat capacity versus temperature with no magnetic field.

The data analysis can often be divided into two parts and different information can be obtained looking at magnetic measurements at high and low temperatures.

Table 3.2 Summary of the magnetic properties. All compounds show antiferromagnetic spin interactions, except for Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$, which is ferromagnetic.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Papper</th>
<th>Magn Ion (spin)</th>
<th>Weiss constant (B)</th>
<th>Tc (K)</th>
<th>µeff (µB)</th>
<th>Metal connection</th>
<th>Frustration parameter f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$Te$_2$O$_6$(PO$_4$)$_2$(OH)$_2$</td>
<td>I</td>
<td>Co$^{2+}$ (3/2)</td>
<td>-10.3(5) K</td>
<td>-20</td>
<td>5.27(1)</td>
<td>chains</td>
<td>-0.5</td>
</tr>
<tr>
<td>Cr$_3$Te$_2$O$_6$Cl$_3$</td>
<td>II</td>
<td>Cr$^{3+}$ (3/2)</td>
<td>-230 K</td>
<td>-34</td>
<td>3.9</td>
<td>chains</td>
<td>-6.8</td>
</tr>
<tr>
<td>Co$_3$(SeO$_3$)$_3$4(PO$_3$OH)$_3$(H$_2$O)</td>
<td>IV</td>
<td>Co$^{2+}$ (3/2)</td>
<td>-76.83(1) K</td>
<td>-16</td>
<td>4.02(3)</td>
<td>framework</td>
<td>-4.8</td>
</tr>
<tr>
<td>Fe$_3$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$</td>
<td>II</td>
<td>Fe$^{2+}$ (4/2)</td>
<td>33.9(3) K</td>
<td>-44</td>
<td>5.27(4)</td>
<td>tubes and chains</td>
<td>-</td>
</tr>
<tr>
<td>Mn$_3$Te$_2$O$_6$(SiO$_4$)$_2$Cl$_2$</td>
<td>V</td>
<td>Mn$^{2+}$ (5/2)</td>
<td>-153(3) K</td>
<td>-4</td>
<td>-5.95</td>
<td>layers</td>
<td>-38</td>
</tr>
<tr>
<td>CuSbO$_6$(SO$_4$)$_2$</td>
<td>X</td>
<td>Cu$^{2+}$ (1/2)</td>
<td>-1.90(5) K</td>
<td>0.67</td>
<td>-1.76</td>
<td>Isolated</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

3.6.1 High temperature magnetic properties

In Figure 3.13 the magnetic susceptibility and the inverse susceptibility is shown for compound Co$_3$(SeO$_3$)$_3$4(PO$_3$OH)$_3$(H$_2$O): the susceptibility was corrected for diamagnetism using tabulated values. Well above the transition temperature for magnetic ordering the magnetic susceptibility follows a Curie Weiss law (Eq.3.1):\[
\chi_{mol} = \frac{C}{T-\theta} \quad \text{(Eq. 3.1)}
\]

By fitting the inverse susceptibility using this linear equation one can calculate the values for the Curie constant (C) and the Weiss temperature (θ). The Weiss constant can also be calculated by extrapolating the linear function of the inverse susceptibility onto the x-axis. Negative Weiss constants indicate an overall antiferromagnetic ordering whereas a positive Weiss constant assumes that ferromagnetic interactions are dominating. Weiss constants of
all compounds are given in Table 3.2. All compounds seem to have an over-
all antiferromagnetic spin coupling except for Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$Cl$_3$, which has
a positive Weiss constant and has therefore ferromagnetic spin interactions.

**Figure 3.13** Magnetic susceptibility (green) and inverse susceptibility (orange) of
Co$_3$(SeO$_3$)$_3$(PO$_4$OH)$_x$(H$_2$O). The dashed line indicates a fit to the Curie-Weiss law extrap-
olated to intercept with the x-axis.

A common way of quantifying the paramagnetic contribution is to calculate
the effective magnetic moment $\mu_{\text{eff}}$:

$$
\mu_{\text{eff}} = \frac{3kT\chi_{\text{mol}}}{N\mu_B} = 2.828\sqrt{T\chi_{\text{mol}}} \quad \text{(Eq. 3.2)}
$$

where $k$ is the Boltzmann constant, $N$ Avogadro’s number and $\mu_B$ the Bohr
magneton. For most of the compounds the effective magnetic moments were
found to be close to a spin only value of $\mu_{\text{eff}} = \sqrt{2S(S+1)}$ assuming a high
spin electronic configuration. Deviations from those values are due to con-
tributions from spin-orbit coupling.

The frustration parameter $f$ in Table 3.2 was calculated from the negative
ratio of the Weiss temperature and the magnetic ordering temperature. With
a remarkable large value of around 38 the compound Mn$_4$(TeO$_3$)(SiO$_4$)Cl$_2$
[Paper V] may have substantial amounts of spin frustration within the ex-
tended manganese oxohalide nets.

### 3.6.2 Low temperature magnetic properties

The critical temperature, below which the spins become magnetically or-
dered, is strongly dependant on the crystal structure and especially on how
the magnetic ions are arranged therein. Among the structures studied in this
work, mainly antiferromagnetic interactions were observed with Neel tem-
peratures well below 50 K. Figure 3.14 shows the magnetic susceptibility...
and heat capacity curves for Co$_3$Te$_2$O$_2$(PO$_4$)$_2$(OH)$_4$. In both curves one can observe two antiferromagnetic transitions around 4 and 20 K originating from magnetic ordering of the two different cobalt sites in the structure.

Figure 3.14  Susceptibility curve and heat capacity measurement for Co$_3$Te$_2$O$_2$(PO$_4$)$_2$(OH)$_4$.

The compound Cr$_3$Te$_5$O$_{13}$Cl$_3$ shows a sharp antiferromagnetic transition around 35 K. This is due to the ordering of the spins from Cr$^{3+}$ that are located in chains of edge sharing [CrO$_6$] octahedra. The transition is very sensitive towards the magnetic field. Figure 3.15 shows the magnetic susceptibility measured at different field strengths. By increasing the field from 0.01 T to 7 T the sharp transition can be suppressed. This can also be seen from the magnetization measurements, revealing a critical field of 0.25 T.

Figure 3.15  (a) Magnetic susceptibility of Cr$_3$Te$_5$O$_{13}$Cl$_3$ at different magnetic fields. The magnetic transition is smeared out with fields above 0.3 T. (b) Magnetization curve. A transition can be observed at around 0.25 T.
During this work nineteen new transition metal oxides and oxohalides containing a lone-pair element have been synthesized and ten of them also contain a tetrahedral building block. Late first row transition metals (Trm) in combination with Se$^{4+}$, Te$^{4+}$ and Sb$^{3+}$ as lone-pair elements (Lp), Cl and Br as halide ions (X) and the tetrahedral building blocks PO$_4$, SiO$_4$, SO$_4$ and VO$_4$ have been studied. Synthesis was performed via chemical reactions in sealed and evacuated silica tubes or via hydrothermal methods. The crystal structures of the new compounds were determined using single crystal diffraction and some of them were also characterized in terms of magnetic properties.

**Synthesis**

High temperature solid-gas reactions in sealed evacuated silica tubes at reaction temperatures in between 500-650 °C was the method of choice for finding new oxohalides. While compounds found in the Trm-Lp-O-X system are normally stable over a wide range of temperatures, the addition of tetrahedral building blocks increased the complexity of the synthesis, and the tolerances in terms of variation in the reaction conditions became smaller. Furthermore, the increased number of combinations of starting materials in different molar ratios makes it more difficult to find new compounds. With hydrothermal synthesis it was only possible to obtain oxide materials, which is due to the high solubility of the halide ions in an aqueous reaction mixture. After finding a new compound the main challenge was to optimize the synthesis conditions in order to obtain phase pure material for further characterization of magnetic properties; for some of the new compounds it was possible, but not for all. In general it was easier to obtain phase pure material from a hydrothermal synthesis as the reaction is normally more homogeneous, and unwanted side products can more easily be washed away.

**Layered oxohalides**

Nine new compounds in the Trm-Lp-O-X system were synthesized. In those compounds the concept of combining lone-pair elements and halide ions in order to find low-dimensional arrangements worked very well. The crystal structures of the new compounds are layered with the transition metal atoms arranged in extended sheets, chains or as isolated entities. The stereochemically active lone-pairs and the halide ions are located in non-
bonded crystal volumes in between the layers and interact through weak van der Waals forces. This weak interaction in between the layers can also be seen from the morphology of the single crystals, which are plate-like due to slow crystal growth along the stacking direction. Due to the very flexible coordination around Mn$^{2+}$, this ion has shown to be an ideal starting point for finding new compounds by simply changing the molar ratios during synthesis. Although this synthesis concept works well for finding new layered materials, it provides little control on the actual arrangement of the transition metal building blocks within the layers.

### Tetrahedral building blocks

Ten new compounds containing phosphate-, silicate-, sulphate- or vanadate groups as tetrahedral building blocks could be synthesized; three of them are oxides and seven are oxohalides. The tetrahedral building blocks are connected to the structural framework by corner sharing and do not polymerize. Compared to the compounds found in the Trm-Lp-O-X system only a few of the compounds containing tetrahedral building blocks were found to be layered; an example is Mn$_4$(TeO$_3$)(SiO$_4$)X$_2$ (X = Br, Cl). Tubular arrangements of the iron atoms are found in the compounds Fe$_7$Sb$_3$(PO$_4$)$_3$O$_6$X$_3$ (X=Cl, Br), and the solid solution Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O) is an open framework compound with small channels. The inclusion of tetrahedral building blocks generally led to unusual crystal structures. Complex hydrogen bonding was observed through the presence of [PO$_3$OH] groups and crystal water in the compound Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O). Unusual solid solutions were obtained when the tetrahedral groups could take the same position as a lone-pair building block within the crystal structure. This led to very special V$^V$/Sb$^{III}$ and P$^V$/Se$^{IV}$ split positions in the compounds Mn$_2$Sb$_{2+x}$(VO$_4$)$_2$.O$_{2+3x}$Cl$_2$ and Co$_3$(SeO$_3$)$_{3-x}$(PO$_3$OH)$_x$(H$_2$O) as the exchanged cations are different in charge and have quite different coordination behavior. Compound Co$_4$Te$_6$(PO$_4$)$_2$O$_6$Cl is built up from charge neutral layers that randomly stack according to two energetically equal stacking positions, which gives rise to diffuse scattering. In general, the inclusion of additional tetrahedral blocks does not necessarily lead to the formation of materials having low-dimensional arrangements even though the tetrahedra act as structural spacers. Nevertheless, the inclusion of such building blocks opens up a new class of compounds having interesting structural arrangements with potentially interesting physical properties.

### Physical properties

Magnetic properties were measured for six compounds for which phase pure material could be synthesized. All the compounds examined except for one were found to undergo antiferromagnetic transitions. The transition temperatures determined by susceptibility curves or heat capacity measurements were found to be well below 50 K. From the value of the frustration parame-
ter f an indication for the presence of geometrical frustration was found in two of the compounds, which can be attributed to the low-dimensional arrangements of the transition metal atoms within the crystal structure.
5. Populärvetenskaplig Sammanfattning

Det här arbetet omfattar syntes, strukturbestämning och karakterisering av magnetiska egenskaper av ett antal nya oxid- och oxohalidfaser som innehåller både övergångsmetaller och så kallade lone-pair element. Joner som har så kallade lone-pair elektoner återfinns i p-blocket i det periodiska systemet och har fyllt s-orbital men inga elekroner i de tillgängliga p-orbitalerna (ns²np⁰). Detta elektronpar deltar inte i kemisk bindning men upptar ungefär samma plats i en kristallstruktur som en syreligand och hjälper till att öppna upp kristallstrukturen. De stereokemiskt aktiva lone-pairelektronerna medför att jonen får en assymetrisk koordination. I oxohalider av den typ som undersöks i det här arbetet hjälper även halidjoner till att öppna upp kristallstrukturen på grund av att dessa har ett lågt kordinationstal. Det har visat sig att kombinationen av joner med ett stereokemiskt aktivt lone-pair och halidjoner är ett framgångsrikt koncept för att hitta nya oorganiska faser som har lågdimensional arranjemang av övergångsmetaller. Med lågdimensionella material menas sådana kristallstrukturer som har vissa byggblok arrangerade i form av skikt, kedjor eller små kluster. Det är framför allt arranjemanget av övergångsmetallerna som är intressant då det är oparade d-elektroner hos dessa som bestämmer den förenings magnetiska egenskaper. I litteraturen finns ett flertal exempel på oorganiska material vars egenskaper beror på det geometriska arranjemanget av övergångsmetaller; tex spinnfrustrerad magnetism där arranjemanget av de magnetiska jonerna är sådant att det finns inslag av både ferromagnetism och antiferromagnetism. Oftast har sådana föreningar valts ut från strukturdatabaser på grund av sin topologi för vidare magnetisk karakterisering och få synteskoncept har presenterats där det är en stor sannolikhet att hitta nya föreningar med sådana egenskaper. Det är mest vanligt med skiktade strukturer i de studerade systemen där övergångsmetallerna bildar kovalenta bindningar till såväl syre som halidjoner (Cl⁻, Br⁻) medan lone-pairkatjonerna oftast enbart binder till syre. Oftast är det enbart svaga Van der Waalsbindningar mellan skikten som inte har någon nettoladdning och halidjonerna och lone-pair elektronerna pekar ut från dessa skikt då det finns plats för dessa i mellanrummen. I det här arbetet beskrivs 19 nya faser varv nio är skiktade strukturer med övergångsmetallerna Mn²⁺, Fe²⁺ och Cr³⁺, lone-pairkatjonerna Te⁴⁺ and Sb³⁺ och halidjonerna Cl⁻ och Br⁻. Inom arbetet har det undersöks hur arranjemanget av övergångsmetalljoner i oxohalider påverkas av att
Inkludera tetradriskt koordinerade byggblock såsom fosfat- (PO$_4$), silikat- (SiO$_4$), sulfat- (SO$_4$) och vanadatgrupper (VO$_4$). Tetredriskt koordinerade byggblock binder oftast vidare till andra byggblock med hörndelning och är därför välkända för att bilda öppna nätverksstrukturer (så kallade open framework compounds). De tetredriskt koordinerade byggblocken har lett till att ett brett spann av olika kristallstrukturer har hittats och bland dessa är det inte enbart skiktade föreningar som hittats utan också öppna nätverk och tubformade arrangemang. Vidare har inkorporeringen av de tetradriska byggblocken medfört att flera nya och ovanliga kristallstrukturer har hittats som har ovanliga fasta lösningar, diffus spridning och komplexa vätebindningar inom strukturerna. Magnetisk karakterisering har gjort av de faser som har kunnat framställas som fasrena material, de flesta av dessa är antiferromagnetiska.
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7. References