A Nuclear Magnetic Resonance Study of Dialkyldithiophosphate Complexes
– Polycrystalline and Surface Adsorbed

Anna-Carin Larsson
DOCTORAL THESIS

A Nuclear Magnetic Resonance Study of Dialkyldithiophosphate Complexes
-Polycrystalline and Surface Adsorbed

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ABSTRACT

$^{31}$P, $^{13}$C and $^{207}$Pb NMR were used to characterize different metal (Ni, Zn, Pb) dialkyldithiophosphate complexes. Eight different sodium or potassium dialkyldithiophosphate salts (alkyl groups R=ethyl-, $n$-propyl, $iso$-propyl, $n$-butyl, $iso$-butyl, sec-butyl, $iso$-amyl and cyclo-hexyl) were used as starting materials. The metal complexes studied are mononuclear, binuclear, tetranuclear or polynuclear and the structural diversity is reflected in different $^{31}$P chemical shifts and chemical shift anisotropies of the complexes. A correlation between the $^{31}$P chemical shift tensor principal value $\delta_{22}$ and the S-P-S angle of the complexes was revealed. The ligands were also adsorbed on the surface of synthetic ZnS and PbS and studied by $^{31}$P CP/MAS NMR: spectra of the dry samples showed that in both cases chemisorption of the ligands on the mineral surfaces occurred. The ligands chemisorbed on ZnS have a bridging coordination, while the coordination of the ligands to PbS is terminal. Products of oxidation and hydrolysis were also found on the mineral surfaces; disulfides were detected on the surface of ZnS and monothiophosphates and orthophosphates on the surface of PbS. After three months of storing of the PbS samples, more hydrolysis products were formed as well as precipitated lead(II) dithiophosphate complexes.

Keywords: $^{31}$P, $^{13}$C, $^{207}$Pb NMR, chemical shift anisotropy, X-ray, dialkyldithiophosphate, nickel(II), zinc(II), lead(II), ab-initio, ZnS, PbS, flotation, coordination, surface adsorption
LIST OF PAPERS

The thesis is based on the following papers:

I Polycrystalline and Surface O, O’-Dialkyldithiophosphate Zinc(II) Complexes: Preparation, ³¹P CP/MAS NMR and Single-Crystal X-Ray Diffraction Studies
A. V. Ivanov, O. N. Antzutkin, A.–C. Larsson, M. Kritikos, W. Forsling

II Correlations Between ³¹P Chemical Shift Anisotropy and Molecular Structure in Polycrystalline O, O’-Dialkyldithiophosphate Zinc(II) and Nickel(II) Complexes: ³¹P CP/MAS NMR and ab-initio Quantum Mechanical Calculation Studies
Journal of the American Chemical Society, accepted

III Complexation of Lead(II) with O, O’-Dialkyldithiophosphate Ligands: ³¹P and ¹³C CP/MAS NMR and Single-Crystal X-Ray Diffraction Studies
Inorganica Chimica Acta, 357, 2004, pp. 2510-2518

IV Solid State ³¹P and ²⁰⁷Pb MAS NMR Study on Polycrystalline O, O’-Dialkyldithiophosphate Lead(II) Complexes
A.–C. Larsson, A. V. Ivanov, W. Forsling, O. N. Antzutkin
Manuscript

V Preparation and Comparative ³¹P CP/MAS NMR Study of Crystalline and Surface (at Synthetic PbS) Lead(II) Complexes with O, O’-Dialkyldithiophosphate Ions
A.–C. Larsson, A. V. Ivanov, O. N. Antzutkin, W. Forsling
Manuscript
Papers related to the subject but not included in the thesis:

**Structural Organization of Zinc, Nickel(II), and Copper(II) O,O´-Dicyclo-hexyl Phosphorodithioate Complexes as Probed by X-Ray Diffraction, EPR, and Solid-State High-Resolution $^{13}$C and $^{31}$P NMR**

**Structural Organization of Nickel(II) and Copper(II) O, O´-Dialkyl Phosphorodithioate Complexes as Probed by Single-Crystal X-ray Diffraction, EPR, and CP/MAS $^{13}$C and $^{31}$P NMR**
Results presented at conferences and meetings

Complexation of Dialkylderivatives of Phosphorus(V) Dithioacids with Zn(II) in Solid State and at a Surface of Synthetic Sphalerite
A.-C. Larsson, Z. Sun, O. N. Antzutkin, W. Forsling, P. Zhukov, A. V. Ivanov

$^{31}$P Chemical Shift Anisotropy of Polycrystalline O, O'-Dialkyldithiophosphate Complexes
A.-C. Larsson, A. V. Ivanov, W. Forsling, O. N Antzutkin
Poster presented at 42nd ENC (Experimental Nuclear Magnetic Resonance Conference), Orlando, Florida, March 11 – 16, 2001

A Nuclear Magnetic Resonance Study on Polycrystalline and Surface O, O'-Dialkyldithiophosphate Complexes
A.-C. Larsson, A. V. Ivanov, O. N. Antzutkin, W. Forsling
Oral presentation at 9th Nordic Symposium on Coordination Chemistry, Umeå, Sweden, June 14-16, 2002

Solid State $^{31}$P and $^{207}$Pb NMR Studies of Pb(II) Dialkyldithiophosphate Complexes, Polycrystalline and Surface Adsorbed on Synthetic Galena (PbS)
A.-C. Larsson, A. V. Ivanov, O. N. Antzutkin, W. Forsling
Poster to be presented at EENC/AMPERE, Lille, France, September 6-11, 2004
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INTRODUCTION

Froth flotation has been used since the beginning of the 20th century as the primary method for enriching and separating sulfide mineral ores. One interesting aspect of the process is the adsorption of collectors on the mineral surface. The aim of the research project presented in this thesis is to investigate if nuclear magnetic resonance (NMR) can be used to determine what types of species are present on the mineral surface after adsorption. It is known that NMR is very sensitive to changes in the electronic environment around the nucleus studied, therefore, in principle, it should be possible to distinguish between different coordination modes of the ligands adsorbed on a mineral surface, as well as to identify possible products of oxidation and hydrolysis. Concentrations of species adsorbed on a mineral surface are naturally very low, which can cause problems with sensitivity, and therefore it is necessary to use an isotope with a high natural abundance. Such an isotope is $^{31}$P, which has 100% natural abundance. Sodium or potassium salts of O, O’-dialkyldithiophosphates are frequently used as collectors of sulfide minerals and as they contain phosphorus nuclei they were suitable systems for NMR investigation.

In order to answer the question of which coordination mode(s) are present on the mineral surface it is important to build up a database of information relevant to the systems studied. To correlate the $^{31}$P chemical shift and $^{31}$P chemical shift anisotropy (CSA) with different structural functions of the ligands, nickel(II), zinc(II) and lead(II) complexes of dithiophosphates with known crystal structure were prepared and studied by solid-state $^{31}$P and $^{207}$Pb NMR. Ab-initio calculations were also performed and used to give a theoretical basis for these correlations. The information from these studies were then used to analyze the surface species and their coordination modes.

To my help in this work Dr. Mikael Kritikos and Dr. Andrey V. Gerasimenko have determined the crystal structures of a few dialkyldithiophosphate complexes and Prof. Angel deDios and M. Sc. Anu Elizabeth Abraham have performed ab-initio quantum mechanical calculations on the dithiophosphates to correlate structural parameters with CSA data.
Overview of papers

As a first step (Paper I) we studied the adsorption of various dialkyldithiophosphates on ZnS using $^{31}$P CP/MAS NMR. This study showed that it was possible to detect the surface species during a reasonable experimental time (up to twenty hours per sample). By comparing the chemical shifts of the surface adsorbed species with the chemical shifts of different polycrystalline zinc(II) dialkyldithiophosphate complexes we drew the conclusion that the dithiophosphate ions build covalent bonds with the surface active sites and form a bridging type of coordination.

The next step of the study (Papers II-IV) was to build up a database of information about $^{31}$P chemical shifts and $^{31}$P chemical shift anisotropies of different metal dithiophosphate complexes. By measuring chemical shifts and chemical shifts anisotropies of phosphorus sites in different complexes a correlation between the S-P-S bond angle and the principal value $\delta_{22}$ of the $^{31}$P chemical shift tensor was revealed. This correlation was also confirmed by quantum mechanical ab-initio calculations (Paper II).

The third step (Paper V) was to study the adsorption of dithiophosphates on PbS. In this study it was shown that the chemical shifts of different surface species (dithiophosphates, monothiophosphates and orthophosphates) differ significantly from each other. The dithiophosphate ions chemisorb to the PbS surface forming a terminal (chelating) type of coordination. For di-iso-propyl and di-iso-butyl dithiophosphates also a bulk precipitate is formed. Some chemisorbed species remain after three months, during which time more precipitate as well as products of hydrolysis and oxidation are formed.
THEORETICAL BACKGROUND

DITHIOPHOSPHATES

Dialkyldithiophosphoric acids or their salts are widely used as collectors in the froth flotation of sulfide minerals, as starting materials for the synthesis of insecticides, fungicides and pesticides, and for vulcanization of rubber. Zinc dithiophosphates are efficient lubricant oil-additives, as they have both anti-oxidant and anti-wear properties.

The dithiophosphates are also interesting systems from the point of view of coordination chemistry, as they can form metal-ligand complexes in which the ligands may display different structural functions, i.e. unidentate, bidentate (both chelating terminal and bridging) or combined tridentate. Therefore, the structures of the complexes can be mono-, bi-, tetra- or polynuclear.
CRYSTAL STRUCTURES

Nickel(II) dialkyldithiophosphates

The crystal structures of *bis*(O, O’-dialkyldithiophosphato-S, S’)nickel(II), [Ni{S$_2$P(OR)$_2$}$]$, are known for R=ethyl [1], *n*-propyl [2], *iso*-propyl [3] and *iso*-butyl [2]. The structures are mononuclear with two structurally equivalent dithiophosphate ligands terminally coordinated to the nickel atom, forming small four-membered Ni-S-P-S rings, see Figure 1. The nickel atom and the four sulfur atoms are in square planar configuration and the phosphorus atom is centered in a tetrahedron with the two sulfur atoms and the two oxygen atoms in the corners. The color of the compounds are deep purple.

![Figure 1. Crystal structure of the central fragment of mononuclear nickel(II) dithiophosphate.](image)

The di-*n*-propyldithiophosphate nickel(II) complex has two structurally non-equivalent molecules in its unit cell, see Figure 2. Each molecule has two structurally equivalent ligands, but the structural data differ between the two molecules in the unit cell. The two ligands in nickel(II) di-*iso*-butyldithiophosphate are slightly nonequivalent.
Figure 2. Crystal structure of the central fragments of the two structurally nonequivalent molecules in the unit cell of the mononuclear di-n-propyldithiophosphate nickel(II) complex.

Table 1 shows molecular structure data of importance for the dialkyldithiophosphate nickel(II) complexes in this study.

Table 1. Molecular structure data for the dialkyldithiophosphate nickel(II) complexes in this study.

<table>
<thead>
<tr>
<th>Complex</th>
<th>P-O (Å)</th>
<th>P-S (Å)</th>
<th>S-P-S (°)</th>
<th>O-P-O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(S₂P(OC₂H₅)₂)₂] [1]</td>
<td>1.579±0.009</td>
<td>1.571±0.009</td>
<td>1.986±0.006</td>
<td>103.1±0.2</td>
</tr>
<tr>
<td>[Ni(S₂P(OC₃H₇)₂)₂] [2]</td>
<td>1.5656±0.0009</td>
<td>1.569±0.001</td>
<td>1.993±0.006</td>
<td>102.09±0.02</td>
</tr>
<tr>
<td>[Ni(S₂P(O-i-C₃H₇)₂)₂] [3]</td>
<td>1.564±0.003</td>
<td>1.566±0.003</td>
<td>1.991±0.002</td>
<td>101.7±0.1</td>
</tr>
<tr>
<td>α-[Ni(S₂P(O-i-C₄H₉)₂)₂] [2]</td>
<td>1.561±0.003</td>
<td>1.565±0.003</td>
<td>1.985±0.002</td>
<td>102.78±0.06</td>
</tr>
<tr>
<td>T &lt; 296K</td>
<td>1.562±0.003</td>
<td>1.565±0.003</td>
<td>1.989±0.002</td>
<td>102.91±0.07</td>
</tr>
</tbody>
</table>
Zinc(II) dialkyldithiophosphates

Table 2 shows the molecular structure data of importance for the dialkyldithiophosphate zinc(II) complexes in this study.

Table 2. Molecular structure data for the dialkyldithiophosphate zinc(II) complexes in this study.

<table>
<thead>
<tr>
<th>Complex</th>
<th>P-O (Å)</th>
<th>P-S (Å)</th>
<th>S-P-S (°)</th>
<th>O-P-O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Zn}{\text{S}_2\text{P(O-OC_2H_5)_2}}_2}_n)</td>
<td>1.57±0.01 (B)*</td>
<td>1.992±0.007 (B)</td>
<td>108.0±0.3 (B)</td>
<td>97.4±0.7 (B)</td>
</tr>
<tr>
<td></td>
<td>1.57±0.01 (B)</td>
<td>2.001±0.005 (B)</td>
<td>109.7±0.4 (T)</td>
<td>94.5±1.2 (T)</td>
</tr>
<tr>
<td></td>
<td>1.56±0.02 (T)*</td>
<td>1.987±0.009 (T)</td>
<td>1.973±0.011 (T)</td>
<td>1.973±0.011 (T)</td>
</tr>
<tr>
<td></td>
<td>1.62±0.02 (T)</td>
<td>1.984±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
</tr>
<tr>
<td>([\text{Zn}_2{\text{S}_2\text{P(O-i-C_3H_7)_2}}_4]</td>
<td>1.60±0.01 (B)</td>
<td>1.957±0.007 (B)</td>
<td>117.3±0.3 (B)</td>
<td>104.4±0.8 (B)</td>
</tr>
<tr>
<td></td>
<td>1.58±0.02 (B)</td>
<td>1.971±0.007 (B)</td>
<td>109.7±0.3 (T)</td>
<td>94.9±0.8 (T)</td>
</tr>
<tr>
<td></td>
<td>1.56±0.01 (T)</td>
<td>1.984±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
</tr>
<tr>
<td></td>
<td>1.57±0.01 (T)</td>
<td>1.984±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
<td>1.968±0.007 (T)</td>
</tr>
<tr>
<td>([\text{Zn}_2{\text{S}_2\text{P(O-c-C_6H_11)_2}}_4]</td>
<td>1.56±0.006 (B)</td>
<td>1.988±0.003 (B)</td>
<td>115.73±0.13 (B)</td>
<td>100.9±0.3 (B)</td>
</tr>
<tr>
<td></td>
<td>1.58±0.005 (B)</td>
<td>1.992±0.003 (B)</td>
<td>1.992±0.003 (B)</td>
<td>1.992±0.003 (B)</td>
</tr>
<tr>
<td></td>
<td>1.56±0.005 (T)</td>
<td>1.995±0.003 (T)</td>
<td>1.992±0.003 (T)</td>
<td>1.992±0.003 (T)</td>
</tr>
<tr>
<td></td>
<td>1.57±0.005 (T)</td>
<td>1.992±0.003 (T)</td>
<td>1.992±0.003 (T)</td>
<td>1.992±0.003 (T)</td>
</tr>
<tr>
<td>([\text{Zn}_4\text{S}_2\text{P(O-OC_2H_5)_2}]_6]</td>
<td>1.60±0.01 (B)</td>
<td>1.983±0.005 (B)</td>
<td>120.5±0.2 (B)</td>
<td>101.6±0.5 (B)</td>
</tr>
<tr>
<td></td>
<td>1.56±0.09 (B)</td>
<td>1.993±0.005 (B)</td>
<td>121.1±0.2 (B)</td>
<td>100±0.1 (B)</td>
</tr>
<tr>
<td></td>
<td>1.53±0.01 (B)</td>
<td>1.981±0.006 (B)</td>
<td>1.968±0.006 (B)</td>
<td>1.968±0.006 (B)</td>
</tr>
<tr>
<td></td>
<td>1.56±0.02 (B)</td>
<td>1.981±0.006 (B)</td>
<td>1.968±0.006 (B)</td>
<td>1.968±0.006 (B)</td>
</tr>
</tbody>
</table>

* (B) = bridging ligands, (T) = terminal ligands

**Binuclear type**

The crystal structures of \(\text{bis[}\mu_2-(O, O’-dialkyldithiophosphato-S, S’)(O, O’-dialkyldithiophosphato-S, S’)]\) \(\text{dizinc(II), [Zn}_2\{\text{S}_2\text{P(OR)}_2\}_2\], are known for R=iso-propyl, [4] and cyclo-hexyl, [I]). The structures are binuclear with two terminal ligands and two bridging ligands, see Figure 3. The terminally chelated type of ligand forms a small four-membered Zn-S-P-S ring, of the same type as in the dithiophosphate nickel(II) complexes while the bridging type of ligand connects the two zinc atoms forming a flexible eight-membered ring. The zinc atoms are in a distorted tetrahedral environment caused by the differences in the two types of ligands coordinated to the zinc atom. The phosphorus atoms are centered in a tetrahedron with the two sulfur atoms and the two oxygen atoms in the corners.
Polynuclear type

The zinc(II) diethylidithiophosphate complex, *catena*-poly[µ₂-O, O’-diethylidithiophosphato]zinc(II), [Zn{S₂P(OC₂H₅)₂}₂]ₙ, [5], consists of a polymeric chain, built up by alternating terminal and bridging ligands in tetrahedral coordination around the zinc atoms, see Figure 4. The phosphorus atoms are centred in a tetrahedron with the two sulfurs and two oxygens in the corners. As in the mononuclear nickel(II) and binuclear zinc(II) dithiophosphate complexes, the terminal ligands in the polymeric zinc(II) species form small four-membered Zn-S-P-S rings.
Tetranuclear type

The molecular structures of hexakis(μ₂-(O, O'-diethylidithiophosphato-S, S')-μ₄-thio-tetrazinc(II), [Zn₄S₂P(OEt)₂]₆ [6], and hexakis(μ₂-(O, O'-dialkyldithiophosphato-S, S')-μ₄-oxo-tetrazinc(II), [Zn₄O₂P₂]₆ [7], (R = iso-propyl and n-butyl) are known. The structures have four zinc atoms tetrahedrally coordinated to a central sulfur or oxygen atom, and connected to six bridging ligands, in which the phosphorus atoms are centred in a tetrahedron with the two sulfurs and two oxygens in the corners, see Figure 5.
Lead(II) dialkyldithiophosphates

Table 3 shows the molecular structure data of importance for the lead(II) dialkyldithiophosphate complexes in this study. In general, the complexes consist of monomeric units with two dithiophosphate ligands terminally coordinated to a lead atom. The coordination of the ligands to the lead atom is somewhat distorted due to the presence of a stereochemically active lone pair of electrons on the lead atom. The phosphorus atoms are centred in a tetrahedron with the two sulfurs and two oxygens in the corners. The monomeric units are connected to neighboring monomers in different ways, giving rise to lead(II) dithiophosphate complexes with three different types of structures; mononuclear, binuclear and polynuclear.
Table 3. Molecular structure data for the dialkyldithiophosphate lead(II) complexes in this study.

<table>
<thead>
<tr>
<th>Complex</th>
<th>P-S (Å)</th>
<th>S-P-S (°)</th>
<th>P-O (Å)</th>
<th>O-P-O (°)</th>
<th>S-Pb (Å)</th>
<th>P-Pb (Å)</th>
<th>P-S-Pb (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pb(S₂P(OC₂H₅)₂)₂] [8]</td>
<td>1.995±0.008; 1.969±0.007</td>
<td>115.4±0.3</td>
<td>1.59±0.2; 1.62±0.2</td>
<td>100.1±0.8</td>
<td>2.75</td>
<td>3.40</td>
<td>83.6*</td>
</tr>
<tr>
<td></td>
<td>1.991±0.009; 1.968±0.007</td>
<td>116.2±0.4</td>
<td>1.61±0.1; 1.59±0.2</td>
<td>105.2±0.9</td>
<td>2.79</td>
<td>3.40</td>
<td>83.1*</td>
</tr>
<tr>
<td>[Pb(S₂P(OC₃H₇)₂)₂] [III]</td>
<td>1.974±0.001; 1.984±0.001</td>
<td>116.16±0.05</td>
<td>1.58±0.002; 1.59±0.002</td>
<td>105.1±0.1</td>
<td>3.21</td>
<td>3.54</td>
<td>93.0*</td>
</tr>
<tr>
<td></td>
<td>1.977±0.001; 1.996±0.001</td>
<td>114.91±0.05</td>
<td>1.58±0.002; 1.57±0.002</td>
<td>100.7±0.1</td>
<td>2.80</td>
<td>3.52</td>
<td>92.9*</td>
</tr>
<tr>
<td>[Pb₂(S₂P(O-i-C₃H₇)₂)₄] [9]</td>
<td>2.000±0.014; 1.982±0.013</td>
<td>113.8±0.6</td>
<td>1.58±0.017; 1.58±0.014</td>
<td>110.5±0.9</td>
<td>3.23</td>
<td>3.56</td>
<td>95.5*</td>
</tr>
<tr>
<td></td>
<td>1.958±0.013; 1.944±0.012</td>
<td>114.6±0.6</td>
<td>1.55±0.017; 1.58±0.016</td>
<td>100.7±0.8</td>
<td>2.77</td>
<td>3.52</td>
<td>94.7*</td>
</tr>
<tr>
<td>[Pb₂(S₂P(O-o-C₆H₁₁)₂)₄] [III]</td>
<td>1.994±0.006; 1.951±0.008</td>
<td>113.9±0.3</td>
<td>1.55±0.02; 1.60±0.01</td>
<td>100.4±0.7</td>
<td>2.76</td>
<td>3.47</td>
<td>92.6*</td>
</tr>
<tr>
<td></td>
<td>1.985±0.007; 1.986±0.008</td>
<td>112.0±0.4</td>
<td>1.57±0.01; 1.56±0.01</td>
<td>97.3±0.10</td>
<td>2.76</td>
<td>3.33</td>
<td>87.4*</td>
</tr>
<tr>
<td>[Pb₂(S₂P(O-i-C₄H₉)₂)₄] [III]</td>
<td>1.994±0.001; 1.994±0.001</td>
<td>114.35±0.05</td>
<td>1.58±0.002; 1.58±0.002</td>
<td>101.0±0.1</td>
<td>3.26</td>
<td>3.61</td>
<td>94.5*</td>
</tr>
<tr>
<td></td>
<td>1.979±0.001; 2.005±0.001</td>
<td>114.14±0.05</td>
<td>1.58±0.002; 1.59±0.002</td>
<td>100.5±0.1</td>
<td>3.10</td>
<td>3.48</td>
<td>92.7*</td>
</tr>
</tbody>
</table>

* Bridging distance (S-Pb' or P-Pb') or bridging bond angle (P-S-Pb')
**Mononuclear type**

*Bis*(O, O’-diethyl dithiophosphato-S, S’)*lead*(II), [Pb{S₂P(OEt)₂}]₂ [8], consists of monomeric units with two slightly nonequivalent ligands. The coordination of the sulfurs to the lead atom is a distorted tetragonal pyramid. The two ligands are bent out of the plane and each monomer is weakly coordinating the neighboring units with Pb–S and Pb–O bonds, building up an infinite chain structure, see Figure 6.

![Figure 6. Weakly associated three-membered fragment of mononuclear lead(II) diethyl dithiophosphate.](image)

**Binuclear type**

The lead(II) *di*-iso-butyldithiophosphate, *bis*[μ₂-(O,O’-dialkyl dithiophosphato-S, S, S’)(O, O’-*di*-iso-butyldithiophosphato-S, S’)]*dilead*(II), [Pb₂{S₂P(O-i-Bu)₂}]₄, [9], consists of a dimeric unit, with two terminal ligands and two ligands with combined structural function, i. e. both terminal and bridging, see Figure 7.
Figure 7. Molecular structure of the central fragment of binuclear lead(II) di-iso-butyl dithiophosphate.

The ligands are bent out of the plane because of the presence of a stereochemically active lone pair of electrons on each lead atom. The coordination of the sulfurs to the lead atom can be described as a distorted square-based pyramid. The central Pb-S-Pb-S part is planar, as well as the four-membered terminal Pb-S-P-S rings.

**Polynuclear type**

A third type of molecular structure present in the lead(II) dialkyldithiophosphate complexes is the polymeric type. These complexes, *catena*-poly[μ₂-O, O’-dialkyldithiophosphato) lead(II)], [Pb(S₂P(OR)₂)₂]ₙ, R=n-propyl [III], i-propyl [10, 11], cyclo-hexyl [III], have ligands with combined structural functions, i.e. they coordinate both terminally chelating to one lead atom and at the same time bridging to the lead atom in the neighboring mononuclear unit. In this way infinite chain structures are built up. The coordination of sulfur atoms around the lead atom is octahedral. The terminal four-membered Pb-S-P-S rings are nearly planar. The di-iso-propyldithiophosphate complex builds chains by coordinating one sulfur of each ligand to the neighboring lead atom, see Figure 8.
Figure 8. Three-membered fragment of the polymeric di-iso-propyldithiophosphate lead(II) complex.

The di-n-propyl and di-cyclo-hexyl dithiophosphate complexes also build chains by coordinating one sulfur of each ligand to the neighboring lead atom, but in these structures one of the oxygens are also weakly coordinated to one of the lead atoms, see Figure 9.
Figure 9. Four-membered fragment of the polymeric di-n-propyl and di-cyclohexylidithiophosphate lead(II) complexes.

Minerals

The crystal structures of sphalerite and galena are cubic, with Zn-Zn distances of 3.84 Å and 5.43 Å and Pb-Pb distances of 4.20 Å and 5.94 Å [12], see Figure 10. Each zinc atom in sphalerite is coordinated to four sulfur atoms, forming a regular tetrahedron. Likewise each sulfur is coordinated to four zinc atoms, also forming a regular tetrahedron. Each lead atom in galena is coordinated to six sulfur atoms forming a regular octahedron and likewise each sulfur is coordinated to six lead atoms.
Figure 10. Crystal structure of sphalerite (ZnS) and galena (PbS) [13].
FLOTATION

Froth flotation is a widely used method of concentrating sulfide ores [14]. In froth flotation, ground ore is added to a water basin and certain chemicals, so called collectors, are added, which adsorb on the mineral surfaces and make them hydrophobic. Air is streamed through the water basin and the mineral particles attach to the air bubbles and gather on the surface of the water basin. The collectors are added in small amounts, only enough for monolayer adsorption, as higher concentrations can reduce the recovery of the minerals.

The most widely used collectors for floating sulfide minerals are xanthates and dithiophosphates [14]. The common feature for those collectors is that they have a polar part, which is attracted to the charged mineral surface, and a non-polar part, consisting of hydrocarbon chains, which are orientated out from the surface and create a hydrophobic film around the mineral particle.

The length of the hydrocarbon chains is important for the hydrophobicity and the adsorption to the surface [14]. Longer hydrocarbon chains increase the hydrophobicity and decrease the solubility of the collector products.
SURFACE ADSORPTION

Mineral surfaces

Sulfide minerals have a very low solubility in water, but in the presence of oxygen the surface can be oxidized [14]. Elemental sulfur may form and at acidic pH metal ions will dissolve from the surface, whereas at neutral and alkaline pH the metal ions will form metal hydroxides. The mineral surface can also be oxidized to oxy-sulfur species, e.g. sulfates and thiosulfates. Those species can make the surface more soluble in aqueous solutions.

Adsorption processes

Chemisorption

Chemisorption means that a chemical bond has been created between a ligand and a surface. The coordination modes can be monodentate, with one bond only between the surface and the ligand, bridging, where the ligand binds to two different metal ions, or terminal, also called chelating, with two bonds to the same metal ion on the surface, see Figure 11 with dithiophosphates as an example.

- Monodentate
- Bridging
- Terminal

Bridging coordination can only occur if the distance between the metal sites is appropriate so that the binding atoms can reach both metal sites. The coordination number of the surface metal sites also determines the coordination mode. For

Figure 11. Different modes of coordination for chemisorbed dithiophosphates; from left to right: monodentate, bridging and terminal (chelating). M = metal site.
terminal coordination to occur, there must be two binding possibilities from the exterior of the mineral surface to the same metal site, whereas for the monodentate and bridging modes it is enough with only one.

**Physisorption**

Physisorption means that only weak electrostatic or van der Waals interaction between the surface and the adsorbed molecules are present. Physisorbed species can be metal-ligand complexes formed by the ligand and metal ions dissolved from the surface, or disulfides, formed by red-ox processes near or at the surface, see Figure 12.

![Figure 12. Different species that can be physisorbed on the surface: a precipitated metal complex or a disulfide.](image)

Slightly soluble carbonates and sulfoxides, which are formed by oxidation of the mineral surface in contact with air or water, dissolve during the flotation and can give a fairly high concentration of metal ions and anions near the surface. If the concentrations of dissolved metal ions and collector ions exceed the solubility product of the precipitate, the metal ions can react with the collector and form a bulk precipitate, which may physisorb on the surface [15]. A chemisorbed ligand can form a metal complex precipitate if it pulls the metal ion away from the surface lattice, or may form a disulfide if it reacts with another collector ion.
Other sorption processes

Depending on the amount of ligands present in the solution, bilayers or micelles can be formed on a mineral surface [16]. Bilayers are formed when the alkyl chains of the ligands interact with the alkyl chains of the monolayer. Micelles are formed if the concentration of the ligand exceeds the critical micelle concentration (CMC), see Figure 13. These sorption processes can prevent flotation because the surface of the particle-collector complex will become charged and hydrophilic.

![Figure 13. Bilayers (a) and micelles (b) formed on a surface.](image-url)
NMR

General theory

The phenomenon of nuclear magnetic resonance (NMR) in the condensed phase (liquid or solid) was first discovered in 1945 by Purcell et al. [17] and by Bloch et al. [18]. The theory and practice of nuclear magnetic resonance has been described in several introductory textbooks [19-23]. NMR is very sensitive to small variations in the electronic environment around the nuclei in a sample, thus making it possible to distinguish between different chemical sites in the sample.

Atomic nuclei possess spin angular momentum, \( I \), also called spin. The spin is quantized, and can only have certain discrete values, \( I = n/2 \); \( n \geq 0 \). In this thesis only nuclei with \( I = 1/2 \) will be considered. Nuclei with \( I \neq 0 \) also have a nuclear magnetic moment, \( \mu \), which is proportional to the spin, \( \mu = \gamma I \). The proportionality constant, \( \gamma \), is called the magnetogyric ratio. Some very common nuclei, like \(^{12}\)C and \(^{16}\)O have \( I = 0 \) in their ground state and, thus, have no magnetic moment. These nuclei are ‘invisible’ in NMR because it is the magnetic moment that gives rise to the resonance signals that are detected. The nuclei to be considered in this thesis are \(^{31}\)P with a natural abundance of 100% and magnetogyric ratio \( \gamma = 1.08394 \times 10^8 \text{s}^{-1} \text{T}^{-1} \), \(^{207}\)Pb with a natural abundance of 22.1% and \( \gamma = 0.55805 \times 10^8 \text{s}^{-1} \text{T}^{-1} \), \(^{13}\)C with a natural abundance of 1.1% and \( \gamma = 0.67283 \times 10^8 \text{s}^{-1} \text{T}^{-1} \) and \(^{1}\)H with a natural abundance of ca. 100% and \( \gamma = 2.67522 \times 10^8 \text{s}^{-1} \text{T}^{-1} \).

The nuclear spins in a sample under consideration interact with externally applied static and oscillating magnetic fields as well as with each other and the electrons in the sample. The total energy of interaction can be described by the Hamiltonian for the spin system:

\[
\hat{H}^{\text{total}} = \hat{H}^{\text{ext}} + \hat{H}^{\text{rf}} = \hat{H}^{Z} + \hat{H}^{\text{rf}} + \hat{H}^{\text{DD}} + \hat{H}^{\tau} + \hat{H}^{J} \tag{1}
\]

The external interactions are the Zeeman interaction \((Z)\) between the magnetic moments and the applied magnetic field and the rf-interaction \((\text{rf})\) which is the
interaction of the magnetic moments with the radio-frequency pulses applied during an experiment. The internal interactions are the dipole-dipole coupling (DD) between the nuclear spins, the shielding interaction ($\sigma$) between the nuclei and the magnetic field created by electrons in the environment, and the spin-spin coupling ($J$) between the nuclear spins through the bonding electrons. Each of the interactions will be described in the following sections. At the high magnetic fields of the NMR spectrometers the Zeeman interaction is the dominant one and the other interactions can be regarded as perturbations of the Zeeman spin states.

**Zeeman interaction**

In the absence of a magnetic field the magnetic moments of the spins $I$ are randomly oriented. When the spins are placed in an external magnetic field their magnetic moments will interact with the field. This interaction gives rise to $2I+1$ different stationary energy levels, the Zeeman eigenstates. The energy for a single isolated spin in a static magnetic field can be expressed by the Zeeman Hamiltonian:

$$\hat{H}^Z = -\gamma I_z B_0$$

For $I = 1/2$ the possible energies are $E = -\mu I B_0 = -\gamma m_I B_0$ where $m_I = \pm 1/2$ are the projections of $I$ on the z-axis in the laboratory reference frame, the direction of the applied magnetic field, $B_0$. The two eigenstates of the spin are denoted $|\alpha\rangle = |+1/2\rangle$ (spin-up) and $|\beta\rangle = |-1/2\rangle$ (spin-down). The difference in energy between the two levels is $\Delta E = E_\beta - E_\alpha = \gamma B_0$.

The spins will precess at a constant angle around the external magnetic field, see Figure 14. The precession frequency, $\omega_0$, also called the Larmor frequency, depends on the strength of the magnetic field and is also related to the difference in energy levels, $\omega_0 = -\gamma B_0 = -\Delta E$. 
After some time $t$, after the application of an external magnetic field $B_0$, see Figure 15, the spin system has reached thermal equilibrium. The spins populate the two Zeeman energy levels according to the Boltzmann distribution. A net magnetization has developed in the system, parallel to $B_0$.

This magnetization is called the longitudinal magnetization, and the time constant describing the rate of relaxation is denoted $T_1$, the spin-lattice or longitudinal relaxation time constant.


**Interaction with radiofrequency pulses**

In the NMR experiment an oscillating radio-frequency pulse \((\omega_{\text{rf}})\) will interact with the nuclear spin magnetic moments and perturb the Boltzmann equilibrium. The Hamiltonian for this interaction, when the pulse is applied along the x-axis in the laboratory reference frame, is:

\[
\hat{H}_{\text{rf}} = -\gamma I_x B_1 \cos(\omega_{\text{rf}} t) = \omega_1 I_x \left( e^{i(\omega_0 t + \phi)} + e^{-i(\omega_0 t + \phi)} \right)/2
\]  

(3)

The magnetic field associated with the rf-pulse is \(B_1\) and \(\omega_1 = -\gamma B_1\).

In order to remove the time-dependence of the Hamiltonian, and simplify the mathematical treatment, it is common practice to describe the interaction between the spins and the rf-field in a rotating frame of reference. This frame rotates around the z-axis at \(\omega_{\text{rf}}\), the frequency of the rf-pulse, and the field associated with the pulse appears to be static, neglecting the second fast oscillating component. The full Hamiltonian in the rotating frame becomes:

\[
\hat{H}^{\text{rf}} + \hat{H}^{\text{Z}} = (\omega_0 - \omega_{\text{rf}}) I_x + \omega_1 I_x / 2
\]  

(4)

The magnetization vector \(M\) will precess around \(B_0\) at frequency \(\Omega_0 = \omega_0 - \omega_{\text{rf}}\) instead of \(\omega_0\). An rf-pulse on resonance with the Larmor frequency \(\omega_0\) will make the magnetization along the z-axis to vanish, since \(\gamma B_0 = \Omega_0 = 0\) and the precession of \(M\) will be determined by \(B_1\), see Figure 16.

If the rf-pulse is off resonance \(\omega_{\text{rf}} \neq \omega_0\) the magnetization will experience a reduced magnetic field along the z-axis, \(B_{\text{red}} = \Omega_0 / \gamma = B_0 [1 - (\omega_{\text{rf}} / \omega_0)]\) and \(M\) will precess around an effective magnetic field \(B_{\text{eff}}\).
Figure 16. In the rotating frame the spin magnetization will precess around an effective magnetic field rather than around $B_0$ [20].

The precession frequency of the spins in the rotating frame is governed by the nutation frequency, $\omega_1 = -\gamma B_1$, which specifies the amplitude of the rf-pulse. The rf-pulse will rotate the magnetization an angle $\theta$ from the z-axis, $\theta = \omega_1 \tau_{rf}$, where $\tau_{rf}$ is the pulse length, typically in microseconds. The usual choice of flip angle is $90^\circ$ because this creates the largest magnitude of magnetization in the $xy$-plane, the plane of detection of the signal, see Figure 17.

Figure 17. An rf-pulse ($\theta = 90^\circ$) along the x-axis rotates the spin magnetization along the $-y$-axis [19].
After the pulse, when $B_1$ ceases, the magnetization is precessing around $B_0(1-\omega_0/\omega_0)$. The magnetization will restore its equilibrium state along $B_0$ through relaxation processes, see Figure 18.

![Image of relaxation processes](image)

**Figure 18.** Relaxation of the magnetization after a radio frequency pulse. (a) the $T_2$ process, all sites have the same resonance frequency, but lose their phase coherence, (b) the $T_1$ process [23].

The magnetization will restore along the $z$-axis with time constant $T_1$ and randomize in the $xy$-plane with a rate determined by the transverse relaxation time constant, $T_2$. The signal from the decaying transverse magnetization is detected as a FID (free induction decay) signal, see Figure 19. The FID is a function of time, and is Fourier transformed into a function of frequencies. The frequencies are then displayed in a spectrum. The linewidths of the signals in the spectrum are proportional to $1/T_2$. This is so called homogeneous broadening. However, there might be additional broadening of the resonance lines due to a distribution of isotropic chemical shifts, (sites with different chemical environment). This type of broadening is called inhomogeneous.

![Image of FID signal](image)

**Figure 19.** FID signal.
The resonance frequencies depend on the strength of the magnetic field, which cause inconveniences if one wishes to compare results from experiments performed on spectrometers with different $B_0$-fields. Therefore the frequencies are usually reported on a relative scale, the chemical shift scale, in which the frequencies of the sample are compared to the frequency of a reference compound. Common reference compounds are 85% H$_3$PO$_4$(aq) for $^{31}$P, Pb(NO$_3$)$_2$ for $^{207}$Pb and TMS (tetramethylsilane) for $^{13}$C and $^1$H. The chemical shift, $\delta$, is reported in ppm (parts per million) and is defined as

$$\delta = (\omega_0 - \omega_{\text{ref}}) \times 10^6 / \omega_{\text{ref}}$$ \hspace{1cm} (5)

A solid state $^{31}$P NMR spectrum of powder lead(II) di-iso-butyldithiophosphate is shown in Figure 20. Reference is set at 85% H$_3$PO$_4$(aq), 0 ppm.

![Single-pulse $^{31}$P NMR spectrum of solid lead(II) di-iso-butyldithiophosphate.](image)

The spectrum in Figure 20 is very broad because each $^{31}$P spin interacts with the other spins, both $^{31}$P and $^1$H, in the system thus causing small perturbations in the energy levels and the resonance frequencies. These internal interactions depend on the distance between the spins, the electronic environment in the vicinity of the spins and the angle between the magnetic field and the axis of interaction.

For samples in the liquid state, where the molecular rotations and tumblings are fast, most of these interactions are averaged out and the spectrum contains only
narrow resonance lines, at frequencies mostly determined by the Zeeman interaction and the isotropic chemical shifts. In a solid the molecules are fixed in a lattice and each nuclear spin will experience a magnetic environment that is slightly different than that from the neighboring nuclei, causing a broadening of the resonance lines. This broadening obscures most of the information about the spin system. In order to remove the different anisotropic interactions and improve the possibility of gaining structural and chemical information, the spin system can be manipulated in different ways.

**Dipole-dipole interaction**

The dominant internal interaction in most spin systems is the direct dipole-dipole interaction. Each nuclear spin is a magnetic dipole and the magnetic field generated in the surrounding space interacts with any neighboring spin, and vice versa, see Figure 21.

![Figure 21. Magnetic field interactions between spins j and k leading to dipole-dipole coupling [19].](image)

The Hamiltonian for the dipole-dipole interaction in a solid is a sum over every spin pair in the sample,

\[ \hat{H}_{dd} = \sum_{j<k} \hat{H}_{jk} \]  

(6)

The Hamiltonian is slightly different for the homonuclear and the heteronuclear cases. The coupling between two spins of the same isotopic species (homonuclear) is
\[ \hat{H}_{jk}^{DD} = d_{jk}(3\cos^2\theta_{jk} - 1)(3\hat{I}_{jz}\hat{I}_{kz} - \hat{I}_j\hat{I}_k) \]  

where \( I_j I_k = I_{jx}I_{kx} + I_{jy}I_{ky} + I_{jz}I_{kz} \) and \( d_{jk} \) is the dipole-dipole coupling constant.

The coupling between spins of different isotopic species (heteronuclear) is given by the so called weak dipole-dipole coupling approximation:

\[ \hat{H}_{jk}^{DD} = d_{jk}(3\cos^2\theta_{jk} - 1) 2 \hat{I}_{jz}\hat{I}_{kz} \]  

Both the homonuclear and the heteronuclear coupling are proportional to \( d_{jk} \), the dipole-dipole coupling constant,

\[ d_{jk} = -\frac{\mu_0\gamma_j\gamma_k\hbar}{8\pi r_{jk}^3} \]  

From the equations it can be seen that the dipole-dipole coupling between two spins depends on the distance between them \( (r_{jk}) \) as well as the angle the vector joining the spins makes to the external magnetic field \( (\theta_{jk}) \). In a powder sample each spin pair has its own axis towards the magnetic field and the perturbation of the Zeeman energy levels will be slightly different for each pair and thus also the resonance frequency, \( \omega_{0j} \). This leads to the broad spectral pattern seen in Figure 20.
**Heteronuclear decoupling**

Protons (\(^1\)H) have a large magnetogyric ratio and gives a large contribution to the dipole-dipole effects on the spectrum of the X-spins. The effect from the protons can be removed by heteronuclear decoupling. This is done by irradiating the sample with an rf-pulse at the proton Larmor frequency at the same time as the X-signals are detected. The protons are rotated 90° along –y in the \(^1\)H rotating frame. Immediately after the initial pulse a second pulse is applied along –y, which spin-locks the proton spins, along –y and decouple them from the phosphorus spins. This removes some of the broadening in the \(^{31}\)P NMR spectrum and more structural features appear, see Figure 22. However, the sharp features in the spectrum are distorted by the ring-down signal of the probe as discussed below.

*Figure 22. Proton decoupled single-pulse \(^{31}\)P NMR spectrum of solid lead(II) di-iso-butyldithio-phosphate.*
**Spin-echoes**

Samples which cover a broad range of resonance frequencies due to the different spin interactions will dephase fast in the xy-plane. The fast decay will lead to very short FIDs. The transmitted rf-pulse usually causes acoustic ringing in the receiver coil so the FID can not be measured until after a short time interval (the dead time of the NMR probe) and for fast decaying FIDs a large part of the signal will be lost. This signal loss causes distortions in the Fourier transformed spectrum. The problem with distortions can be overcome by recording an echo signal instead [24], see Figure 23.

![Spin-echo pulse sequence](image)

**Figure 23. Spin-echo pulse sequence [20].**

A 90°-pulse along the x-axis will put the transverse spin magnetization along the –y-axis. The spins start to dephase in the xy-plane due to their different offset frequencies ($\Omega_0$). The spins with positive offset frequencies rotate anti-clockwise and the spins with negative offset frequencies rotate clock-wise. After a time interval $\tau$, a second pulse will rotate the magnetization vectors 180° around the y-axis. The spins interchange places so the spins with positive offset frequencies now move towards the spins with negative offset frequencies and after a time $\tau$ the spins are refocused along the y-axis and continues their dephasing. By choosing $\tau$ to be longer than the dead time of the coil the whole FID can be recorded. Figure 24 shows a proton-decoupled $^{31}$P spin-echo spectrum of lead(II)
di-iso-butyldithiophosphate. (Note that the sharp features seen in the spectrum in Figure 22, caused by the ring-down signal from the probe, are now absent.)

Figure 24. Proton decoupled $^{31}P$ NMR spin-echo spectrum of solid lead(II) di-iso-butyldithiophosphate.

**Chemical shift anisotropy**

The spectrum in Figure 24 is broad because there are still internal spin interactions left in the sample. The broad features remaining arise from the chemical shift anisotropy of the phosphorus sites in the sample.

Each nucleus is surrounded by electrons. The electrons are charged and in the presence of an external magnetic field the electrons start to circulate, generating a small magnetic field, $B'$, which shields the nucleus from the external field. The Hamiltonian for this interaction is:

$$\hat{H}^\sigma = -\gamma \hat{I} \sigma \hat{B}_0$$

(10)

Thus, the actual field experienced by the nucleus is $B = B_0 - B' = B_0(1 - \sigma)$ where $\sigma$ is the shielding tensor, and the resonance frequency will be $\omega = -\gamma B$. The local
magnetic field will vary depending on the electronic environment in the vicinity of the nucleus. Nuclei around which the electron density is high will be more shielded and the resonance frequency will be smaller than in nuclei where the electron density is smaller, e.g. methyl-carbons have higher electron density than carbons bonded to an electronegative atom like oxygen, which pulls the electrons away from the carbon atom, leaving it more deshielded. This difference in electron distribution is the basis for the chemical shift, $\delta$. Furthermore, the electron distribution around a nucleus in a molecule is generally not spherically symmetric, so the magnitude of the shielding will depend on the orientation of the molecule with respect to $B_0$, the so called chemical shift anisotropy. The shielding can be expressed as a Cartesian tensor, a $3 \times 3$ matrix which describes the directional dependence of the shielding:

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

The elements of the shielding tensor are here expressed in a general reference frame. The matrix element $\sigma_{xx}$ represents the shielding in the direction of the x-axis when $B_0$ is applied along the x-axis in the same frame, $\sigma_{xy}$ represents the shielding in the direction of the y-axis when $B_0$ is applied along the x-axis, and so on.

To a good degree of approximation the chemical shift tensor (CST) is related to the shielding tensor so that $\delta = -\sigma$. The definition of the chemical shift was given above (eq. 5), $\delta = (\omega_0 - \omega_{rel}) \times 10^6 / \omega_{rel}$, where $\omega_0$ is the Larmor frequency of the spin of interest and $\omega_{rel}$ is the Larmor frequency of the spins in the reference compound (85% H$_3$PO$_4$ for $^{31}$P). The resonance frequency due to shielding becomes $\omega = -\gamma B$ where $B = B_0(1-\sigma)$. The shielding is expressed relative to that of a bare nucleus, ($\sigma_{\text{bare}} = 0$). Inserted in the above expression for the chemical shift, with the bare nucleus as the reference, this gives:
\[
\delta = \frac{(\omega - \omega_{\text{bare}})}{\omega_{\text{bare}}} = \frac{(1 - \sigma - (1 - \sigma_{\text{bare}}))}{(1 - \sigma_{\text{bare}})} = \frac{-\sigma + \sigma_{\text{bare}}}{(1 - \sigma_{\text{bare}})} = -\sigma
\]  

(12)

A tensor described in one frame can be transformed to any other frame by an appropriate transformation matrix. The tensor in the principal axis frame (PAF) is diagonal and the three values on the diagonal are called the principal values, denoted \(\delta_{xx}, \delta_{yy}\) and \(\delta_{zz}\). They describe the shielding characteristics of the molecule and are orthogonal. A single crystal can be placed at certain angles relative to the external magnetic field and be described in the laboratory frame. The shielding tensor, and hence the chemical shift, for each orientation will change due to the orientational dependence of the shielding, but the transformation to the PAF will always yield the same three principal values.

A powder consists of many crystallites randomly distributed over all possible orientations relative to \(B_0\). This leads to a powder pattern, with a large number of overlapping resonance peaks, see Figure 25. From molecular symmetry certain orientations give the same chemical shift and this leads to an increased intensity of the powder pattern at that frequency.

Figure 25. A powder pattern formed from crystallites with different orientations relative to \(B_0\) [19].

The discontinuities are the principal values of the tensor, the diagonal elements of the tensor in its principal axis frame (PAF), and defines the most deshielded, the most frequent and the most shielded chemical shifts, respectively. In liquid samples where the molecules tumble fast over all orientations the anisotropy averages to zero and only a narrow resonance line appears for each spin site. The position of this line is called the isotropic chemical shift and it can be determined
from a powder pattern as the trace of the tensor, $\delta_{\text{iso}} = (\delta_{xx} + \delta_{yy} + \delta_{zz}) / 3$. The trace of the tensor is the same irrespective of which axis frame is used for the definition of the tensor.

There are different conventions for reporting the chemical shift anisotropy and the principal values of the tensor. The principal values are reported according to their shielding. In the chemical shift scale the least shielded spins (highest resonance frequency) are on the left and the most shielded (lowest resonance frequency) appear to the right, $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. In the shielding scale the least shielded spins are also to the left, but here $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ because of the opposite signs of the values, see Figure 26.

![Diagram](image)

Figure 26. The principal values of the anisotropy tensors in the chemical shift (deshielding) and shielding scales, respectively, can be determined from the three singularities in the powder pattern (a static NMR spectrum).

The span is defined as $\Omega = \delta_{11} - \delta_{33}$ and the skew $\kappa = 3(\delta_{22} - \delta_{\text{iso}}) / \Omega$. The chemical shift anisotropy can be determined by $\delta_{\text{aniso}} = (\delta_{zz} - \delta_{\text{iso}})$ and the asymmetry parameter by $\eta = (\delta_{xx} - \delta_{yy}) / \delta_{\text{aniso}}$. In the latter convention the principal values are ordered as $|\delta_{zz} - \delta_{\text{iso}}| \geq |\delta_{xx} - \delta_{\text{iso}}| \geq |\delta_{yy} - \delta_{\text{iso}}|$. 
For axially symmetric tensors, see Figure 27, two of the principal values are the same and the notation in this case is $\delta_\|$, which is associated with the magnetic field along the unique principal axis and $\delta_\perp$ for the magnetic field perpendicular to this axis. For axially symmetric tensors $\eta = 0$.

![Figure 27. Powder pattern for an axially symmetric chemical shift tensor.](image)

Shielding tensors and how changes in the molecular geometry alters their shape can be calculated theoretically by *ab-initio* quantum mechanical calculation methods. The magnetic field and the magnetic moments cause perturbations of the molecular energy and these perturbations define the shielding. The components of the shielding tensor can be derived from $\sigma_{ij} = \frac{\partial^2 E}{\partial B_i \partial B_j}$ [25-26]. The energy, $E$, describes the total energy of the molecule. The Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{V}_{\text{nuc}} + \hat{V}_{\text{ele}} + \hat{V}_{\text{int}}$$

where $T$ is the kinetic energy and $V$ is the potential energy of the nuclei (n) and electrons (e) respectively [27]. Each of the energy terms is a sum over all nuclei or electrons in the molecule and each electron and nucleus is described by a wavefunction, $\Psi$, given by a linear combination of atomic orbitals. These orbitals in turn are described by a linear combination of exponential functions, which describe the radial and spatial distributions of the orbital. After having found the coefficients of the orbitals corresponding to the lowest molecular energy the
expression is differentiated with respect to the magnetic field and the magnetic moment to give the elements of the shielding tensor.

**Magic angle spinning**

In cases where the sample contains overlapping powder patterns from nuclei with different CSA, as in Figure 24, it can be difficult to determine the principal CST values for different chemical sites. In these cases magic-angle-spinning (MAS) can assist in solving the problem. Recall that in liquid solutions the fast rotational tumbling of the molecules will average the internal spin-spin interactions discussed. By mechanically rotating the solid sample at a certain angle \( \theta_m \) relative to the external magnetic field the internal second rank tensorial interactions can be averaged to zero. The average chemical shift for a rotating spin is equal to

\[
\delta = \delta_{\text{iso}} + (3\cos^2\theta_m - 1) \times \left[ (3\cos^2\beta - 1)(\delta_{33} - \delta_{\text{iso}}) + \cos^2\beta \cos^2\alpha (\delta_{11} - \delta_{22}) \right] / 4
\]  

(14)

where \( \alpha \) and \( \beta \) are the angles specifying the orientation of the PAF in the frame of the spinning system [28]. When the term \( 3\cos^2\theta_m - 1 \) equals zero, the anisotropic contribution to the chemical shift will vanish and only the isotropic part will remain. This happens for \( \theta_m = 54.74^\circ \), the magic angle. The signal-to-noise ratio will improve because all the signal intensity is collected in the narrow resonance line at the isotropic shift. Rotation will also cause the dipole-dipole interactions, also a second rank tensorial interaction, to vanish, which further narrows the resonance lines.

If the spinning speed \( \omega_r \) is slower than the CSA (for \( ^{31}\text{P} \) in the dithiophosphates \( \Omega \omega_0 \approx 25 \text{ kHz} \) and for \( ^{207}\text{Pb} \approx 250 \text{ kHz} \) the isotropic chemical shift will be flanked by spinning sidebands, at frequencies \( \pm \omega_r \), see Figure 28.
To be able to distinguish which of the resonance peaks are at the isotropic chemical shifts, it is necessary to spin to sample at a few different rotor frequencies. The spinning sidebands spread out with increasing rotor speed, while the isotropic shifts remain at the same positions, see Figure 29.

From the intensities of the spinning sidebands it is possible to recover the principal values of the chemical shift tensor [29]. The intensities are complicated...
functions of the chemical shift parameters and by numerical integration of the
functions it is possible to obtain the span and the skew.

Cross-polarization

A way to enhance the sensitivity of nuclei with low magnetogyric ratio is by using
cross-polarization (CP) between two different spin systems [30]. Protons which
have a high natural abundance and high magnetogyric ratio can be used to transfer
magnetization to other spins increasing their signal strength. In addition, protons
usually relax faster than other spins, which would allow shorter pulse delays
between acquisitions of the signal transients. The cross-polarization technique is
especially useful for spin systems which have a low natural abundance and long
T₁ relaxation times. A pulse sequence for the cross-polarization experiment is
shown in Figure 30.

Figure 30. Cross polarization experiment [21].

A 90° pulse at the resonance frequency of the protons is applied along the x-axis
in the rotating frame of the protons (I), creating transverse magnetization of the
protons along –y. In the next step these spins are locked along –y by applying
another pulse parallel to the magnetization (along –y). During the spin locking
period (τ_{cp}) an rf-pulse at the resonance frequency of the S-spin is applied along -y
in the rotating frame of the S-spins. By adjusting the strengths of the rf-pulses for
the I-spins and the S-spins to satisfy the Hartmann-Hahn condition, $γ_I B_{1I} = γ_S B_{1S}$,
it is possible to transfer magnetization between the spin systems. After the mixing
period the S-spins are allowed to decay and the FID is recorded while the protons are decoupled, to avoid spin interactions leading to line broadening.

The Hartmann-Hahn condition ensures that the two spin systems have the same energies and the same precession frequencies. At the beginning of the pulse the S-spins have almost no spin polarization (the number of $|\alpha\rangle$ spins is almost equal to the number of $|\beta\rangle$ spins). During the contact time ($\tau_{cp}$) the S-spins couple to the proton spins and mutual spin flips occur. The spin flips occur spontaneously in abundant spin systems where the nuclei are close enough to each other to couple effectively. However, for rare spins the distances between spins are too long for effective coupling to occur. In the cross polarization experiment where the energy levels of the I and S spins are made equal, the rare S spins can effectively couple to the more abundant I spin system, thus exchanging energy through spin flips. For each S spin flipping from $|\beta\rangle$ to $|\alpha\rangle$ a proton spin flips from $|\alpha\rangle$ to $|\beta\rangle$, see Figure 31. Energy is transferred from the proton system to the S-spin system, keeping the total energy conserved.
After rotation along \( x \) the effect from \( B_0 \) disappears and the magnetization is determined by \( B_1 \), which is much weaker. The polarization of the magnetization is determined by the magnetogyric ratio and the magnetic field strength, so the proton spins will relax to satisfy the new equilibrium condition, according to the rotating frame relaxation time, \( T_{1p} \). After the contact time the spin systems are allowed to relax and the FID of the S-spins is acquired. The spectrum will have
stronger signals by a factor $\frac{\gamma_I}{\gamma_S}$ due to the increased build-up in magnetization. The spectrum of lead(II) di-iso-butyldithiophosphate after a CP/MAS experiment is shown in Figure 32.

![Figure 32. CP/MAS $^{31}$P NMR spectrum with proton decoupling of solid lead(II) di-iso-butyldithiophosphate under magic-angle-spinning ($\nu_r=2000$ Hz).](image)

Magic angle spinning at high speeds can interfere with the cross polarization because high spinning speeds tend to suppress the heteronuclear dipole-dipole interaction which is needed for the cross polarization to be efficient.

The length of the contact time is important for the result of the cross-polarization efficiency. Too short contact times will not give enough polarization transfer to give strong signals and too long contact times will diminish the optimum signal due to $T_{1P}$ relaxation. The stronger the coupling between I and S the faster the polarization transfer is. Short contact times will preferentially transfer polarization between spins very close to each other ($r_{\text{short}}$) and as the contact time increases also more distant spin pairs can get a transfer of polarization. The different polarization times lead to different relative signal intensities for nuclei in different chemical environments.
**Spin-spin interaction**

The narrow resonance lines in the spectrum in Figure 32 reveals yet another interaction between spins, the spin-spin coupling, also called J-coupling or scalar coupling. This interaction is seldomly seen in spectra of solid samples because the line widths are usually too large. The Hamiltonian for the interaction is

\[ \hat{H}_s = 2\pi \hat{J}_{jk} \hat{I}_j \hat{I}_k \]  

(15)

where \( \hat{J}_{jk} \) is the J-coupling tensor for the coupling between the two spins \( I_j \) and \( I_k \). The coupling depends on the electronic density at the nuclei and in their vicinity.

Spin \( j \) magnetizes the electrons in the molecule and this magnetization is transferred through chemical bonds to any neighboring spin \( k \). Spin \( k \) magnetizes the spin \( j \) in the same way. These magnetic fields are not averaged out by molecular tumbling (in liquids or during MAS) since they are distributed through the chemical bonds between the interacting nuclei.

Depending on whether the two spins are parallel or anti-parallel in the external magnetic field the energy is lowered or raised, relative to the case where there are no J-coupled nuclear spin. The result is a splitting of the chemical shift resonance line, see Figure 33.
Lead has three isotopes, $^{206}$Pb, $^{207}$Pb and $^{209}$Pb. Only $^{207}$Pb have spin $I \neq 0$ (natural abundance 22%, $I = 1/2$) so 78% of the $^{31}$P nuclei have no lead nuclear spin to interact with and thus the $^{31}$P resonance lines are at the isotropic chemical shifts for these isotopomers. Only 22% of the $^{31}$P signal is split by J-coupling with $^{207}$Pb, (11% of the spins have slightly higher energy and 11% slightly lower energy).

The most important mechanism for J-coupling is the Fermi contact interaction ($J^C$). A nucleus A with spin-$1/2$, which is not coupled to any neighboring nucleus, will have a chemical shift position defined by the difference in energy between the two spin states $|\alpha\rangle$ and $|\beta\rangle$, see Figure 34a. When the nucleus is coupled to another spin-$1/2$ nucleus, B, the spin states of A will split depending on the relative orientations of the spins, see Figure 34b. For a spin with positive magnetogyric ratio the transition leading to anti-parallelization of the two spins leads to a lower energy, and hence a lower resonance frequency, while the transition leading to parallelization of the spins leads to a higher energy and higher resonance frequency. Addition of yet another spin B will cause further splitting of the energy levels, see Figure 34c. Two of the states are degenerate, giving a resonance line of twice the intensity of the outer resonances.
The Fermi contact interaction takes place between the nucleus and the s-electrons, see Figure 35. The size of $J^c$ depends on the s-electron density at the nuclei. Bonding electron pairs must have opposite spins (Pauli principle), leading to two different electron states, up-down and down-up. When the nuclear spin is zero both electron states are degenerate (Figure 35a). When a nuclear spin interacts with the electrons the electron states split into two different energy levels (Figure 35b). Anti-parallel spins between nuclear and electron spins are more favorable when the magnetogryric ratio of the nucleus is positive. When a second nuclear spin is added the most favorable spin polarizations are when the nuclear spins are anti-parallel, because then both nuclear spins have the favorable anti-parallel polarization to the electrons (Figure 35c).
Figure 35. The mechanism of electron-mediated spin-spin coupling. a) No nuclear spin, b) one nuclear spin, c) two nuclear spins [19].

The p- and d-electrons can also be involved in the coupling mechanism. The orbital term, $J^0$, and the dipolar term, $J^D$, in the J-coupling Hamiltonian depend on the distance between the nuclei and their neighbor p- and d-electrons. These terms describe the interaction of the nucleus with the orbital motion of the electrons.

The additional subsplitting between the two energy levels due to the spin-spin coupling is the J-coupling constant, measured in frequency units (Hz), and is independent of the magnetic field strength. The coupling can be effective over several chemical bonds, the number of bonds is usually given as an index, $^nJ$. Generally $^1J >> ^3J > ^2J > ^4J$. The J-coupling constants depend on several structural factors, e. g. an increase in coordination number reduces J, because the s-electrons are distributed over more bonds. An increase in bond length decreases J as the coupling depends on the nuclear-electron distance, as $1/r^3$. An increased bond angle increases $^2J$. For heavy elements J increases due to relativistic effects since the J-coupling depends mostly on the s-electrons, which are close to the nucleus where the electrons move fast.
MATERIALS AND METHODS

MATERIALS

Metal complexes

The dialkyldithiophosphate nickel(II), zinc(II) and lead(II) complexes were prepared by mixing aqueous solutions of sodium or potassium dithiophosphate salts from CHEMINOVA AGRO A/S with aqueous solutions of NiCl₂, ZnCl₂ and Pb(NO₃)₂ respectively, according to previous methods [4, 5, 8-11, 31]. The alkyl groups of the dithiophosphate salts used were ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, iso-amyl and cyclo-hexyl. The complexes were filtered off, washed with water and dried in air. In cases of structurally disordered systems which showed broad 3¹P CP/MAS NMR resonance lines, the samples were additionally recrystallized from chloroform. Oil-like or initially liquid complexes were separated by extraction into chloroform with subsequent evaporation of the solvent under slight heating.

The tetranuclear zinc(II) complexes were prepared by mixing an aqueous solution of dithiophosphate salt and NaOH with ZnCl₂ [6, 7, 32]. The alkyl groups of the dithiophosphate salts were ethyl, n-propyl, iso-propyl and n-butyl. The complexes were recrystallized from chloroform.

The tetranuclear zinc(II) di-n-propyl and di-n-butyl dithiophosphate complexes were also formed spontaneously from the liquid binuclear zinc(II) complexes as a result of oxidation by atmospheric oxygen after six weeks of storage of the latter complexes in air:

\[2\text{[Zn}_2\text{S}_2\text{P(OR)}_2\text{]}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{[Zn}_4\text{O}\text{S}_2\text{P(OR)}_2\text{]}_4 + (\text{RO})_2\text{P(S)}\text{SS(S)P(OR)}_2\]

The tetranuclear complexes were then separated from the disulfide by washing with absolute ethyl and methyl alcohol, respectively, and recrystallized from chloroform.
Most of the samples were characterized by elemental analysis and/or by $^{13}$C CP/MAS NMR [I, III, IV, 2].

**Sulfide minerals**

The ZnS was prepared by passing H$_2$S gas through an aqueous solution of Zn(NO$_3$)$_2$. The precipitate was centrifuged, washed and dried under nitrogen.

The PbS was prepared by mixing warm (70°C) aqueous solutions of Pb(NO$_3$)$_2$ and Na$_2$S.xH$_2$O (x=7-9). The precipitate was filtered, washed and dried in a desiccator.

BET measurements showed a surface area of 115 m$^2$/g for the synthetic ZnS and 40 m$^2$/g for the synthetic PbS. X-ray powder diffraction showed that the samples were of the sphalerite and galena type.

**Surface complexes**

Surface complexes were prepared by adding 1 g ZnS or PbS to an aqueous solution of a dithiophosphate salt, at pH≈9.0. The concentrations of the solutions were between 3-9 mM in the ZnS experiments and 2-3 mM in the PbS experiments. Deionized water was used and pH was adjusted by NaOH and HCl. The amount of ligand was calculated in each case to give no more than a theoretical monolayer adsorption. The suspensions were stirred for one-two hours and thereafter centrifuged, washed and dried in a desiccator.
METHODS

NMR

The NMR experiments were performed on a Varian/Chemagnetics Infinity and Infinity Plus CMX-360 spectrometer with a magnetic field strength of 8.46 T. The $^{31}$P operating frequency was 145.73 MHz, the $^{207}$Pb frequency was 75.28 MHz, and the $^{13}$C frequency was 90.52 MHz. As an external $^{31}$P reference phosphoric acid (85%) was used, ($\delta_{\text{iso}} = 0 \text{ ppm}$) [33], for $^{13}$C adamantane was used ($\delta_{\text{iso}} = 38.56 \text{ ppm}$ for the most deshielded resonance, relative to TMS) [34] and for the $^{207}$Pb experiments solid Pb(NO$_3$)$_2$ was used, ($\delta_{\text{iso}} = -3492.5 \text{ ppm}$, 292 K) [35].

Liquid state experiments

Liquid state $^{31}$P spectra were recorded using a 10 mm liquid probe. The WALTZ-16 pulse sequence was used [36], with and without proton decoupling. The proton $\pi/2$ pulse was 90 $\mu$s. The samples were dissolved either in deionized water or chloroform.

CP/MAS

Powder samples of polycrystalline or surface adsorbed dithiophosphates were packed in 7.5 mm ZrO$_2$ rotors. $^{31}$P CP/MAS experiments [30] were performed with $\pi/2$ pulses of 5-5.5 $\mu$s, CP contact time 1-5 ms and nutation frequency for protons during decoupling of 64 kHz. 4-256 transients spaced by a relaxation delay of 2-5 s were accumulated for the crystal complexes and 3000-23000 transients spaced by a relaxation delay of 3 s were accumulated for the surface complexes. The magic-angle-spinning frequencies ranged from 1 to 6 kHz.

$^{13}$C CP/MAS experiments were performed with $\pi/2$ pulses of 4.5 $\mu$s, CP contact time 2 ms and $^{13}$C nutation frequency of 58 kHz. 256-10000 transients spaced by a relaxation delay of 2 s were accumulated. The magic-angle-spinning frequencies ranged from 4 to 5.5 kHz.
Single-pulse experiments

Powder samples of lead(II) dialkyldithiophosphates were packed in 4 mm ZrO$_2$ rotors. $^{207}$Pb single-pulse experiments with proton decoupling were performed with $^{207}$Pb 20° pulses of 0.65 µs. Ca. 20000 transients spaced by a relaxation delay of 8 s were accumulated. In order to determine the isotropic chemical shift spectra were acquired at two different spinning frequencies: 11.3 and 12 kHz.

Spin-echo

An Oldfield-echo pulse sequence [37], modified with cross-polarization and proton decoupling was used to obtain static $^{31}$P powder spectra. The $\pi$/2 pulse was 5 µs, the $\pi$ pulse was 10 µs and the echo delay was 100 µs. From 128-1024 transients spaced by a relaxation delay of 3 s were accumulated. The spectra were processed after left shifting the FID to the maximum of the echo signal.

CSA

Simulations of the chemical shift anisotropy (CSA) were performed for the samples at two different spinning speeds by using a Mathematica program developed by Levitt et al. [38]. The program is based on an analysis of spinning sideband intensities, similar to the one of Herzfeld and Berger [29]. Input data are the integrated intensities of the spinning sidebands, the number of the sidebands, the Larmor frequency, the magic-angle-spinning frequency and the noise variance. The program calculates $\chi^2$-plots of the two parameters $\delta_{\text{aniso}}$ and $\eta$ and display them as confidence plots, see Figure 36.
Figure 36. $\chi^2$-confidence plot of the chemical shift parameters $\delta_{\text{aniso}}$ and $\eta$. 95.4% (dashed line) and 68.3% (solid line) joint confidence limits, respectively, for potassium di-iso-propyldithiophosphate.

From the parameters $\delta_{\text{aniso}}$ and $\eta$ and the isotropic chemical shift ($\delta_{\text{iso}}$), the principal values, $\delta_{xx}$, $\delta_{yy}$ and $\delta_{zz}$, of the chemical shift tensor can be calculated, according to the following equations:

\[
\delta_{xx} = \left[ \delta_{\text{iso}} - \frac{\delta_{\text{aniso}} (\eta+1)}{2} \right] \quad (16)
\]

\[
\delta_{yy} = \delta_{xx} + \eta \delta_{\text{aniso}} \quad (17)
\]

\[
\delta_{zz} = \delta_{\text{iso}} + \delta_{\text{aniso}} \quad (18)
\]

with $\delta_{\text{iso}}$, $\delta_{\text{aniso}}$ and $\eta$ defined as

\[
\delta_{\text{iso}} = \frac{\delta_{xx} + \delta_{yy} + \delta_{zz}}{3} \quad (19)
\]
\[ \delta_{\text{aniso}} = \delta_{zz} - \delta_{\text{iso}} \]  

(20)

\[ \eta = \frac{\delta_x - \delta_y}{\delta_{\text{aniso}}} \]  

(21)

\( \delta_{xx}, \delta_{yy} \) and \( \delta_{zz} \) are defined according to \( \left| \delta_{zz} - \delta_{\text{iso}} \right| \geq \left| \delta_{xx} - \delta_{\text{iso}} \right| \geq \left| \delta_{yy} - \delta_{\text{iso}} \right|. \) Values of \( \delta_{\text{aniso}} \) and \( \eta \) from simulations at two different spinning frequencies were obtained and their mean and statistical errors were calculated by using the following equations:

\[ x_{\text{mean}} = \frac{x_m s_n + x_n s_m}{s_m + s_n} \]  

(22)

and

\[ s^2_{\text{mean}} = s^2_{\text{biso}} + \frac{\left( s_{\delta_{\text{aniso}}} (\eta + 1) \right)^2 + \left( s_{\delta_{\text{aniso}}} \eta \right)^2}{4} \]  

(23)

where \( x \) is either \( \delta_{\text{aniso}} \) or \( \eta \) and \( s_m \) and \( s_n \) are the confidence intervals of \( x \) for simulations at two different spinning frequencies with \( m \) and \( n \), respectively, equal to the number of spinning sidebands used in the simulations for each spinning frequency. A two-tailed F-test was performed to confirm that the CSA values obtained from spectra measured at two different spinning frequencies did not differ significantly from each other [39].

The principal values \( \delta_{xx}, \delta_{yy} \) and \( \delta_{zz} \) are complicated functions of \( \delta_{\text{iso}}, \delta_{\text{aniso}} \) and \( \eta \) and the confidence intervals were calculated from the above equations and the partial derivative method [40], giving rise to the following equations:
Orientation of $^{31}$P CST

*Ab-initio* quantum mechanical calculations on a model $[O_2PS_2]^-$ fragment [II] defined the directions of the $^{31}$P chemical shielding tensor principal axes in the molecular frame, see Figure 37.

\[
\begin{align*}
S_{\delta xx}^2 &= S_{\delta iso}^2 + \frac{[S_{\delta aniso}(\eta+1)]^2 + (s_{\eta} \delta_{aniso})^2}{4} \\
S_{\delta yy}^2 &= S_{\delta xx}^2 + (s_{\eta} \delta_{aniso})^2 + (s_{\delta aniso} \eta)^2 \\
S_{\delta zz}^2 &= S_{\delta aniso}^2 + S_{\delta iso}^2
\end{align*}
\]

Figure 37. Model $[O_2PS_2]^-$ fragment used in ab-initio quantum mechanical calculations.

The most shielded component, $\sigma_{33}$, bisects the S-P-S angle, $\sigma_{22}$ is perpendicular to this axis, pointing out of the plane of the S-P-S angle and $\sigma_{11}$, the most deshielded component, is orthogonal to both of these vectors. When a metal atom is bonded to this fragment, the orientation of the tensor slightly changes. An attempt was made to calculate those changes from the optimized single crystal data, used in the calculations.
The unit vector \( \mathbf{\sigma}_{33} \) bisecting the S-P-S angle was calculated as

\[
\frac{[\mathbf{PS1} + \mathbf{PS2}]}{|\mathbf{PS1} + \mathbf{PS2}|}
\]

(27)

where \( \mathbf{PS1} \) and \( \mathbf{PS2} \) are the vectors defining the two PS-bonds, see Figure 38.

\[\sigma_{11}\]

\[\sigma_{33}\]

\[\sigma_{22}\]

\[P\]

\[S1\]

\[S2\]

\[\mathbf{P}, \mathbf{S1} \text{ and } \mathbf{S2} \text{ atoms; they are perpendicular to each other and can be calculated from the two unit vectors } \mathbf{(PS1) \text{ and } \mathbf{(PS2)}}.\]

The unit vector \( \mathbf{\sigma}_{11} \) is perpendicular to the \( \mathbf{\sigma}_{33} \) vector, in the same plane, and is given by

\[
\frac{[\mathbf{PS1} - \mathbf{PS2}]}{|\mathbf{PS1} - \mathbf{PS2}|}
\]

(28)

The third unit vector \( \mathbf{\sigma}_{22} \) is orthogonal to the other two vectors \( \mathbf{\sigma}_{11} \) and \( \mathbf{\sigma}_{33} \):

\[
\mathbf{\sigma}_{11} \cdot \mathbf{\sigma}_{22} = 0
\]

(29)

\[
\mathbf{\sigma}_{22} \cdot \mathbf{\sigma}_{33} = 0
\]

(30)

\[
\mathbf{\sigma}_{22} \cdot \mathbf{\sigma}_{22} = 1
\]

(31)
The distortions from this geometry are calculated as

\[ \sigma_{nn} \cdot \sigma_{ab}^{nn} = |\sigma_{nn}| |\sigma_{ab}^{nn}| \cos \theta_{nn} \]  

(32)

where \( \sigma_{nn} \) are the vectors in the undistorted geometry, as calculated above, and \( \sigma_{ab}^{nn} \) are the vectors given from the \textit{ab-initio} quantum mechanical calculations, see Figure 39.

![Figure 39 (See text for definitions).](image)

The distortions from the tetrahedral geometry of the O$_2$PS$_2$ molecular fragment can also be calculated. In a regular tetrahedron the two vectors \( S1S2 \) and \( O1O2 \) should be perpendicular and therefore, have a scalar product of zero. The deviation from this angle can be determined as

\[ \theta = \arccos \left( \frac{S1S2 \cdot O1O2}{|S1S2| |O1O2|} \right) \]  

(33)
RESULTS AND DISCUSSION

POLYCRYSTALLINE DITHIOPHOSPHATE COMPLEXES

Isotropic chemical shifts

Figure 40 shows representative $^{31}$P isotropic chemical shifts of the different types of dithiophosphates in this study.

The $^{31}$P chemical shift of the ionic salt, potassium diethyldithiophosphate, (Figure 40a) is more deshielded than the chemical shifts of the covalent metal complexes (Figures 40b-e). The nickel(II) di-iso-propyldithiophosphate has one resonance.
line only, indicating that the two ligands in the mononuclear complex are equivalent. The binuclear zinc(II) di-iso-propyldithiophosphate has two $^{31}$P resonances. This complex consists of two types of ligands, one of which is terminal, analogously with the ligands in the nickel(II) dithiophosphate, and the other type is bridging, connecting the two zinc atoms in the complex. The tetranuclear zinc(II) di-\textit{n}-butyldithiophosphate complex has only the bridging type of ligand. The lead(II) di-cyclo-hexyldithiophosphate complex, has two ligands with combined structural functions, i.e. they are both terminal and bridging, because of the high coordination number of the lead atoms (five or six). Judging from the positions of the resonance lines only, it is reasonable to assign the most shielded resonance line in the binuclear zinc complex to the terminal type of ligand and the less shielded to the bridging type of ligand. However, it has been shown that for cadmium(II) dialkyldithiophosphate complexes the bridging type of ligand is more shielded than the terminal type [41]. Therefore, $^{31}$P CSA was also used in the assignment, as will be discussed later in this thesis.

Another way to assign the chemical shifts of the binuclear zinc complexes is by studying them in the liquid state. It is known that in organic solvents these complexes are reversibly dissociated into the mononuclear species [4], see Figure 41.

![Figure 41 Chemical equilibrium between the dimeric and monomeric forms of zinc(II) dialkyldithiophosphate complexes.](image)

56
If the chemical exchange between the two forms is faster than the NMR time scale (i.e. the difference in isotropic chemical shifts for the $^{31}$P chemical sites, given in frequency units), the separate chemical shifts of the two forms will not be resolved. Only one resonance line will be seen in the spectrum, at the position which is defined by the fractional populations (p) of the two species and their individual chemical shift positions, $\delta = p_1 \delta_1 + p_2 \delta_2$, where $p_1 + p_2 = 1$. As the zinc dithiophosphates in this study contain several different resonances (two terminal in the mononuclear form and two terminal and two bridging in the binuclear form) the expression becomes more complicated [I]:

$$\delta_{av} = p_M \frac{1}{2} \sum_{i=1}^{2} \delta_i^M(\text{term}) + p_B \frac{1}{4} \sum_{i=1}^{2} [\delta_i^B(\text{term}) + \delta_i^B(\text{brid})]$$

(34)

$p_M$ and $p_B$ are the fractional populations of the mononuclear (M) and binuclear (B) forms, respectively ($p_M + p_B = 1$), and $\delta_i^M$ and $\delta_i^B$ are the chemical shifts of the terminal and bridging ligands in the mononuclear and binuclear forms, respectively.

Taking zinc di-iso-propyldithiophosphate as an example, the chemical shift changes towards more shielded values when the concentration of the species in chloroform is lowered, see Table 4. In highly diluted solutions the monomeric species is dominating, and as the resonance position is more shielded at low concentrations, this indicates that this resonance corresponds to the terminal ligands, and the more deshielded one to the bridging ligands.

Table 4 $^{31}$P chemical shifts of zinc(II) di-iso-propyldithiophosphate in chloroform.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>95.4</td>
</tr>
<tr>
<td>0.35</td>
<td>94.9</td>
</tr>
<tr>
<td>0.035</td>
<td>93.4</td>
</tr>
<tr>
<td>&lt;0.005</td>
<td>92.7</td>
</tr>
</tbody>
</table>

57
The di-cyclo-hexylidithiophosphate lead(II) complex is polymeric and has two tridentate ligands, one with mainly bridging character and the other with mainly terminal character, and we suggest that also in this compound the most shielded resonance is from the ligand with largest terminal character.

The spectra of the diethyl- and di-iso-butyldithiophosphate lead(II) complexes have an additional splitting in the resonance lines due to $^2$J-coupling between $^{31}$P and $^{207}$Pb($I=1/2$), see Figure 42. This splitting can be used to additionally support the suggested assignment that the more shielded chemical shift belongs to the terminal type of ligand in the lead(II) dialkyldithiophosphate complexes.

![Figure 42 Central regions (centrebands) in $^{31}$P CP/MAS NMR spectra of lead(II) di-iso-butyl a) and diethyl b) dithiophosphates showing $^2$J-coupling between $^{31}$P and $^{207}$Pb.](image)

The J-coupling in the diethyldithiophosphate lead(II) complex, (Figure 42b) is ca. 80 Hz doublets, i. e. two satellites which flank the central line, with integral ratio of the lines in each multiplet ca. 1:7:1, corresponding to the natural abundance of $^{207}$Pb (22%). This is J-coupling between $^{31}$P and $^{207}$Pb within the terminal ligands, consisting of four-membered P-S-Pb-S rings. The coupling constant for the more shielded resonance of the di-iso-butyldithiophosphate lead(II) complex (Figure 42a) is ca. 140 Hz, a multiplet 1:7:1. The coupling pattern for the other resonance
in the di-iso-butyldithiophosphate complex is more complicated, depending on the presence of different paths for the coupling, and must come from the ligand with combined structural function, see Figure 43. This is an interesting case, seldomly seen in solid state NMR due to the lack of resolution.

![Figure 43](image)

*Figure 43 The $^2J(^{31}P, ^{207}Pb)$-coupling in ligands of the lead(II) di-iso-butyldithiophosphate with combined structural function can occur through different paths, each with its own value of the coupling constant.*

The central resonance line at 98.1 ppm stems from $^{31}P$ nuclei in isotopomers (molecules with different combination of different isotopes) with only non-magnetic lead isotopes (i.e. either $^{206}Pb$ or $^{208}Pb$). This central line is split by ca. 310 Hz due to J-coupling between $^{31}P$ and $^{207}Pb$ (I=1/2) within the terminal path of the complex. The relative probability for such isotopomers is 22%, giving rise to a 1:7:1 multiplet. The central line is additionally split (ca. 56 Hz) by $^3J$-coupling in isotopomers in which the other lead atom (Pb’) in the molecule is magnetic, leading to a bridging path for the coupling. The relative probability for such isotopomers is also 22%, giving rise to a 1:7:1 multiplet. The doublet ($^3J$=310 Hz) is additionally split into a doublet by the presence of isotopomers in which both lead atoms are magnetic ($^{207}Pb$). Since the probability of having two $^{207}Pb$-atoms within the same molecule is only ca. 5% the intensity of this subsplitting is small (1:7:1 in each satellite).
Chemical shift anisotropy

As the chemical shift anisotropy (CSA) can give more information about the chemical environment around the nucleus studied than the isotropic chemical shifts alone it can be of interest to investigate also the CSA of the dithiophosphate complexes. Figure 44 shows static powder patterns representative for the different types of potassium, nickel and zinc dithiophosphates in this study.

![Figure 44](image)

It can be seen that the potassium salts (Figure 44a) and the terminal nickel(II) (Figure 44b) dithiophosphates have almost axially symmetric tensors ($\eta = 0$), but with different signs of the skew ($\kappa \approx +1$ for the potassium salts and $\kappa \approx -1$ for the nickel(II) complexes, respectively), while the tetranuclear zinc(II) dithiohosphate (Figure 44d) with bridging ligands have $\kappa \approx 0$ and $\eta \approx 1$. The spectrum of the zinc(II) diethyl-dithiophosphate complex (Figure 44c) has two overlapping
powder patterns, one with a shape similar to the powder pattern of the nickel dithiophosphate and the other more similar to the powder pattern of the tetranuclear zinc(II) dithiophosphate complex.

It is possible to determine the CSA principal values from the singularities in the powder patterns, however, as can be seen in the spectrum of the zinc(II) diethyldithiophosphate complex (Figure 44c), when two powder patterns overlap it is not so simple to determine the correct values of the CST principal values. If there are more than two powder patterns overlapping, the results will no longer be reliable.

By using the magic-angle-spinning technique the static powder patterns will transform into spinning sideband patterns with centrebands at the isotropic chemical shifts, flanked by a number of spinning sidebands. From the intensities of the spinning sidebands it is possible to estimate the principal values of the CST even for compounds with many different chemically nonequivalent sites.
Potassium dialkyldithiophosphate salts

Figure 45 shows the $^{31}$P CP/MAS NMR spectra of three different potassium dialkyldithiophosphate salts. The shapes of the spinning sideband patterns are almost identical in all three spectra and the span of the spectra are ca. 200 ppm.

Table 5 shows the $^{31}$P chemical shift data for the potassium dialkyldithiophosphate salts in this study. The spectra display either one or two isotropic chemical shifts in the range 104-115 ppm and in most cases the ligands are almost axially symmetric ($\kappa = +1$, $\eta = 0$ and $\delta_{\text{aniso}} < 0$).
Table 5. Chemical shift data of the potassium dialkyldithiophosphates in this study. 95.4% joint confidence limit

<table>
<thead>
<tr>
<th>Salt</th>
<th>δ\text{iso} (ppm)</th>
<th>δ\text{aniso} (ppm)</th>
<th>η</th>
<th>δ_{11} (ppm)</th>
<th>δ_{22} (ppm)</th>
<th>δ_{33} (ppm)</th>
<th>ν (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS₂P(OC₂H₅)₂</td>
<td>108.5±0.1</td>
<td>-107.6±1.0</td>
<td>0.10±0.06</td>
<td>167.7±3.2</td>
<td>156.8±7.0</td>
<td>0.9±1.0</td>
<td>2+3</td>
</tr>
<tr>
<td>KS₂P(OC₃H₇)₂</td>
<td>114.7±0.1</td>
<td>-105.9±2.6</td>
<td>0.08±0.13</td>
<td>172.1±7.2</td>
<td>163.4±15.9</td>
<td>8.8±2.6</td>
<td>2+4</td>
</tr>
<tr>
<td>KS₂P(O-i-C₃H₇)₂</td>
<td>111.7±0.1</td>
<td>-104.7±1.3</td>
<td>0.32±0.03</td>
<td>180.6±1.8</td>
<td>147.6±3.6</td>
<td>7.0±1.3</td>
<td>2+4</td>
</tr>
<tr>
<td>KS₂P(OC₄H₉)₂</td>
<td>115.4±0.2</td>
<td>-106.4±4.0</td>
<td>0.17±0.15</td>
<td>177.4±8.2</td>
<td>159.8±17.7</td>
<td>8.9±4.0</td>
<td>2+4</td>
</tr>
<tr>
<td>KS₂P(O-i-C₅H₁₁)₂</td>
<td>109.9±0.2</td>
<td>-123.0±2.0</td>
<td>0.01±0.14</td>
<td>173.0±8.6</td>
<td>171.8±19.0</td>
<td>-12.2±2.0</td>
<td>2+4</td>
</tr>
<tr>
<td>KS₂P(O-s-C₅H₁₁)₂</td>
<td>114.8±0.6</td>
<td>-112.4±1.7</td>
<td>0.33±0.04</td>
<td>189.5±2.7</td>
<td>152.6±5.5</td>
<td>2.4±1.9</td>
<td>3+4</td>
</tr>
<tr>
<td>KS₂P(O-c-C₆H₁₁)₂</td>
<td>113.8±0.4</td>
<td>-114.0±1.0</td>
<td>0.28±0.03</td>
<td>186.8±1.7</td>
<td>154.7±3.5</td>
<td>-0.2±1.1</td>
<td></td>
</tr>
<tr>
<td>KS₂P(O-i-C₆H₁₃)₂</td>
<td>108.8±0.5</td>
<td>-120.1±2.2</td>
<td>0.09±0.09</td>
<td>174.2±5.7</td>
<td>163.5±12.6</td>
<td>-11.3±2.2</td>
<td>2+4</td>
</tr>
<tr>
<td>Mean*</td>
<td>110.9±3.9</td>
<td>-111.6±5.8</td>
<td>0.17±0.11</td>
<td>176.2±7.8</td>
<td>157.3±14.1</td>
<td>-0.7±7.0</td>
<td></td>
</tr>
</tbody>
</table>

*The statistical mean of the parameters

Nickel(II) dialkyldithiophosphates

Figure 46 shows the $^{31}$P CP/MAS NMR spectra of three different polycrystalline dialkyldithiophosphate nickel(II) complexes. The shapes of the spinning sideband patterns are almost identical in all three cases, and the span is equal to ca. 100 ppm.

Table 6 shows the $^{31}$P chemical shift data for the dialkyldithiophosphate nickel(II) complexes in the study. The chemical shifts are in the range 91-98 ppm, i.e. the phosphorus sites are more shielded in the nickel dithiophosphate compounds than in the potassium dialkyldithiophosphate salts. Contrary to the potassium salts, for nickel dithiophosphates $\kappa < 0$ and $\delta_{\text{aniso}} > 0$. 

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The single $^{31}$P resonance in most of the cases reflects the mononuclear structure of the complexes with two chemically equivalent dialkyldithiophosphate ligands. The nickel di-$n$-propylthiophosphate is also mononuclear, but the unit cell contains two structurally nonequivalent molecules [2] giving rise to two different phosphorus sites with different isotropic chemical shifts, see Table 1, for the molecular structure data. $\alpha$-nickel(II) di-$iso$-butyldithiophosphate also has two resonance lines, assigned on the basis of X-ray data to two nonequivalent ligands in the same molecule.
Table 6. Chemical shift data of the dialkyldithiophosphate nickel(II) complexes in this study, 95.4% joint confidence limit

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ\text{iso} (ppm)</th>
<th>δ\text{aniso} (ppm)</th>
<th>η</th>
<th>δ\text{1} (ppm)</th>
<th>δ\text{2} (ppm)</th>
<th>δ\text{3} (ppm)</th>
<th>ν (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni{S₂P(OC₂H₅)₂}₂]</td>
<td>93.1±0.1</td>
<td>58.4±0.4</td>
<td>0.35±0.04</td>
<td>151.5±0.4</td>
<td>74.2±2.9</td>
<td>53.7±1.3</td>
<td>3+6</td>
</tr>
<tr>
<td>[Ni{S₂P(OC₃H₇)₂}₂]</td>
<td>94.8±0.1</td>
<td>55.3±0.8</td>
<td>0.40±0.03</td>
<td>150.2±0.8</td>
<td>78.2±1.8</td>
<td>56.1±0.9</td>
<td>1+3</td>
</tr>
<tr>
<td>[Ni{S₂P(OC₅H₅)₂}₂]</td>
<td>93.7±0.1</td>
<td>53.5±0.8</td>
<td>0.41±0.03</td>
<td>147.1±0.8</td>
<td>77.9±1.8</td>
<td>55.9±0.9</td>
<td></td>
</tr>
<tr>
<td>[Ni{S₂P(O-i-C₃H₇)₂}₂]</td>
<td>93.3±0.1</td>
<td>60.8±0.9</td>
<td>0.48±0.05</td>
<td>154.1±0.9</td>
<td>77.4±3.2</td>
<td>48.5±1.5</td>
<td>2+4</td>
</tr>
<tr>
<td>[Ni{S₂P(OC₄H₉)₂}²]</td>
<td>93.0±0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-[Ni{S₂P(O-i-C₄H₉)₂}₂]</td>
<td>97.9±0.1</td>
<td>59.4±0.5</td>
<td>0.17±0.06</td>
<td>63.0±1.9</td>
<td>73.3±4.2</td>
<td>157.2±0.5</td>
<td>2+3</td>
</tr>
<tr>
<td>T &lt; 296 K</td>
<td>96.0±0.1</td>
<td>57.7±0.5</td>
<td>0.05±0.03</td>
<td>65.9±0.9</td>
<td>68.5±2.0</td>
<td>153.7±0.5</td>
<td></td>
</tr>
<tr>
<td>β-[Ni{S₂P(O-i-C₄H₉)₂}₂]</td>
<td>93.9±0.1</td>
<td>54.6±0.6</td>
<td>0.43±0.06</td>
<td>148.6±0.6</td>
<td>78.2±3.5</td>
<td>54.9±1.6</td>
<td>3+6</td>
</tr>
<tr>
<td>T &gt; 313 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni{S₂P(O-s-C₄H₉)₂}₂]</td>
<td>92.6±0.6</td>
<td>63.6±1.4</td>
<td>0.40±0.10</td>
<td>156.2±1.6</td>
<td>73.6±7.5</td>
<td>48.1±3.5</td>
<td>3+6</td>
</tr>
<tr>
<td>[Ni{S₂P(O-i-C₅H₁₁)₂}₂]</td>
<td>94.9±0.2</td>
<td>55.4±0.8</td>
<td>0.31±0.07</td>
<td>149.4±0.8</td>
<td>76.1±4.4</td>
<td>59.2±2.0</td>
<td>2+3</td>
</tr>
<tr>
<td>[Ni{S₂P(O-c-C₆H₁₁)₂}₂]</td>
<td>90.7±0.2</td>
<td>55.9±1.4</td>
<td>0.54±0.12</td>
<td>146.6±1.4</td>
<td>77.9±7.6</td>
<td>47.5±3.5</td>
<td>3+6</td>
</tr>
<tr>
<td>Mean***</td>
<td>93.4±1.3</td>
<td>57.1±3.6</td>
<td>0.42±0.07</td>
<td>150.5±3.8</td>
<td>76.7±5.6</td>
<td>53.0±3.5</td>
<td></td>
</tr>
</tbody>
</table>

* Liquid

** Irreversible phase transition α → β at T > 313 K [2]

*** Statistical mean of parameters for these complexes

**Zinc(II) dialkyldithiophosphates**

Figure 47 shows ³¹P CP/MAS NMR spectra of three different zinc(II) dialkyldithiophosphate complexes in this study. The spectra show two groups of isotropic chemical shifts, one representing the terminal type of ligands, and the other representing the bridging type of ligands.
Figure 47. $^{31}$P CP/MAS NMR spectra of polycrystalline polynuclear zinc(II) diethyl a), and binuclear di-iso-propyl b) and di-iso-butyl c) dithiophosphate complexes at spinning frequency 3 kHz. Centrebands are marked by *.

The two groups of phosphorus sites, terminal or bridging, have approximately the same span, ca. 100 ppm, but the shape of their spinning sideband patterns differ, being almost the mirror image of each other. The shape for the most shielded phosphorus sites ($\delta \approx 90$ ppm) is similar to the shape of the spinning sideband pattern of the nickel(II) dialkyldithiophosphates, which have only terminal ligands.

Table 7 shows the $^{31}$P chemical shift data for the binuclear zinc(II) dialkyldithiophosphate complexes in this study.
Table 7. Chemical shift data of the binuclear dialkyldithiophosphate zinc(II) complexes in this study, 95.4% joint confidence limit.

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ_{iso} (ppm)</th>
<th>δ_{aniso} (ppm)</th>
<th>η</th>
<th>δ_{11} (ppm)</th>
<th>δ_{22} (ppm)</th>
<th>δ_{33} (ppm)</th>
<th>ν_{r} (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(S_2P(OC_2H_5)_2)_2]_n</td>
<td>99.7±0.2</td>
<td>46.0±0.8</td>
<td>0.76±0.09</td>
<td>145.7±0.8</td>
<td>74.6±5.0</td>
<td>59.1±2.2</td>
<td>3+6</td>
</tr>
<tr>
<td>[Zn_2(S_2P(OC_2H_5)_2)_4]</td>
<td>100.5±0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn_2(S_2P(O-i-C_3H_7)_2)_4]</td>
<td>97.2±0.1</td>
<td>-54.2±1.4</td>
<td>0.17±0.34</td>
<td>128.9±9.4</td>
<td>119.7±21.1</td>
<td>43.0±1.4</td>
<td>3+6</td>
</tr>
<tr>
<td>[Zn_2(S_2P(O-O-C_4H_9)_2)_4]</td>
<td>100.5±0.1</td>
<td>-57.0±1.8</td>
<td>0.34±0.12</td>
<td>142.0±3.6</td>
<td>112.4±2.5</td>
<td>49.5±0.8</td>
<td>2+3</td>
</tr>
<tr>
<td>Mean terminal***</td>
<td>96.6±2.0</td>
<td>53.1±4.1</td>
<td>0.19±0.14</td>
<td>149.6±4.5</td>
<td>75.0±8.9</td>
<td>65.1±4.8</td>
<td></td>
</tr>
<tr>
<td>Mean bridging****</td>
<td>100.5±2.8</td>
<td>-53.4±4.5</td>
<td>0.35±0.12</td>
<td>136.5±5.3</td>
<td>118.0±8.6</td>
<td>47.1±5.3</td>
<td></td>
</tr>
</tbody>
</table>

* Liquid
** Phase transition from a low temperature conformation with C_1 symmetry to a high temperature distorted conformation
*** Statistical mean of parameters for the terminal ligands
**** Statistical mean of parameters for the bridging ligands (data for [Zn(S_2P(OC_2H_5)_2)_2]_n were omitted because of its polynuclear structure).
One of the phosphorus sites in each pair has $\delta_{\text{aniso}} > 0$ and the other $\delta_{\text{aniso}} < 0$, except for the zinc(II) diethyldithiophosphate, for which both terminal and bridging ligands have $\delta_{\text{aniso}} > 0$. Considering the similarities in shape of the spinning sideband pattern and the sign of $\delta_{\text{aniso}}$ between the nickel dialkyldithiophosphate complexes and the most shielded resonances of the zinc dithiophosphates, the suggestion is that these resonances can be assigned to phosphorus sites in the terminal ligands and hence, the other resonance lines are assigned to the bridging ligands. It is worth noting that the molecular structure of the diethyldithiophosphate compound [5] differs from that of the other zinc(II) dithiophosphates in this study [1, 4], being polymeric instead of binuclear.

The tetranuclear zinc(II) dialkyldithiophosphate complexes have only bridging ligands. $^{31}$P CP/MAS NMR spectra of three different tetranuclear zinc(II) dithiophosphates are shown in Figure 48.

![Figure 48. $^{31}$P CP/MAS NMR spectra of polycrystalline tetranuclear diethyl a), di-n-butyl b) and di-iso-propyl c) dithiophosphate zinc(II) complexes at spinning frequency 3 kHz. Centrebands are marked by *.

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The shapes of the spinning sideband patterns are similar in all three spectra, and also similar to the shapes of the bridging ligands in the binuclear zinc(II) dithiophosphate complexes. The span is ca. 110 ppm.

Table 8 shows the $^{31}$P chemical shift data for the tetranuclear zinc complexes.

Table 8. Chemical shift data of the tetranuclear dialkyl-dithiophosphate zinc(II) complexes in this study, 95.4% joint confidence limit

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\delta_{\text{aniso}}$ (ppm)</th>
<th>$\eta$</th>
<th>$\delta_{11}$ (ppm)</th>
<th>$\delta_{22}$ (ppm)</th>
<th>$\delta_{33}$ (ppm)</th>
<th>$\nu_r$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Zn}_4\text{O}{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2}_6]$</td>
<td>102.2±0.6</td>
<td>-58.4±4.6</td>
<td>0.82±0.11</td>
<td>155.2±5.2</td>
<td>107.5±8.9</td>
<td>43.7±4.7</td>
<td>2+3</td>
</tr>
<tr>
<td>$[\text{Zn}_4\text{O}{\text{S}_2\text{P}(\text{OC}_3\text{H}_7)_2}_6]$</td>
<td>102.7±0.4</td>
<td>-59.1±1.5</td>
<td>0.74±0.15</td>
<td>154.1±4.7</td>
<td>110.4±10.2</td>
<td>43.7±1.5</td>
<td>2+3</td>
</tr>
<tr>
<td>$[\text{Zn}_4\text{O}{\text{S}_2\text{P}(\text{OC}_4\text{H}_9)_2}_6]$</td>
<td>100.2±0.5</td>
<td>-60.6±3.1</td>
<td>0.70±0.10</td>
<td>151.6±4.1</td>
<td>109.5±7.8</td>
<td>39.7±3.1</td>
<td>2+3</td>
</tr>
</tbody>
</table>

$^*$ The spectrum contains two groups of resonance lines with three resonances in each group, 98.7, 99.0, 99.1 and 100.0, 100.3, 100.5. In this study the CSA values $\delta_{\text{aniso}}$ and $\eta$ were simulated by integrating over each group.

$^{**}$ Statistical mean of parameters for these complexes.

Mean**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\delta_{\text{aniso}}$ (ppm)</th>
<th>$\eta$</th>
<th>$\delta_{11}$ (ppm)</th>
<th>$\delta_{22}$ (ppm)</th>
<th>$\delta_{33}$ (ppm)</th>
<th>$\nu_r$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean**</td>
<td>101.5±1.7</td>
<td>-59.5±2.5</td>
<td>0.74±0.06</td>
<td>153.2±4.6</td>
<td>109.1±5.3</td>
<td>42.0±3.0</td>
<td></td>
</tr>
</tbody>
</table>
**Lead(II) dialkyldithiophosphates**

Figure 49 shows $^{31}\text{P}$ CP/MAS NMR spectra of three different lead(II) dialkyldithiophosphate complexes. The spectra generally have two different resonances, and a span of ca. 150 ppm. The shapes of the spinning sideband patterns are similar in all cases except for the most shielded phosphorus site in the di-iso-butyldithiophosphate complex, which seems to be almost a mirror image of the other patterns, see Figure 49a.

![NMR Spectra](image)

*Figure 49 $^{31}\text{P}$ CP/MAS NMR spectra of polycrystalline binuclear di-iso-butyl a), polynuclear di-n-propyl, b) and mononuclear diethyl c) dithiophosphate lead(II) complexes at spinning frequency 3 kHz. Centrebands are marked by *. 

Table 9 shows the chemical shift data for the different dialkyldithiophosphate lead(II) complexes. It can be seen that the $^{31}\text{P}$ CSA parameter $\delta_{\text{aniso}} < 0$ in all cases except for the most shielded resonance of the lead(II) di-iso-butyldithiophosphate.
Table 9. Chemical shift data of the lead(II) dialkyldithiophosphates in this study, 95.4% joint confidence limit

<table>
<thead>
<tr>
<th>Complex</th>
<th>δiso (ppm)</th>
<th>zJ* (Hz)</th>
<th>δaniso (ppm)</th>
<th>η</th>
<th>δ11 (ppm)</th>
<th>δ22 (ppm)</th>
<th>δ33 (ppm)</th>
<th>νr (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pb{S2P(O-C2H5)2}2]2+</td>
<td>98.5±0.1</td>
<td>83</td>
<td>-76.4±1.2</td>
<td>0.38±0.06</td>
<td>151.0±2.4</td>
<td>122.3±5.1</td>
<td>22.1±1.2</td>
<td>2+4.7</td>
</tr>
<tr>
<td></td>
<td>97.2±0.1</td>
<td>79</td>
<td>-66.0±1.3</td>
<td>0.69±0.05</td>
<td>153.0±2.0</td>
<td>107.3±4.0</td>
<td>31.2±1.3</td>
<td></td>
</tr>
<tr>
<td>[Pb{S2P(O-C3H7)2}2]n</td>
<td>98.1±0.1</td>
<td>-66.6±0.9</td>
<td>0.64±0.04</td>
<td>152.8±1.4</td>
<td>110.0±2.8</td>
<td>31.6±1.0</td>
<td>2+4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>97.3±0.1</td>
<td>-78.6±0.9</td>
<td>0.22±0.05</td>
<td>145.1±2.2</td>
<td>128.0±4.8</td>
<td>18.7±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb{S2P(O-C4H9)2}2]n</td>
<td>96.5±0.2</td>
<td>-60.1±1.3</td>
<td>0.83±0.05</td>
<td>151.6±1.8</td>
<td>101.5±3.5</td>
<td>36.4±1.4</td>
<td>2+4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96.2±0.2</td>
<td>-57.7±1.0</td>
<td>0.86±0.04</td>
<td>149.7±1.5</td>
<td>100.3±2.9</td>
<td>38.4±1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb{S2P(O-C5H11)2}2]n</td>
<td>100.0±0.2</td>
<td>-69.3±1.9</td>
<td>0.60±0.07</td>
<td>155.5±2.8</td>
<td>113.8±5.5</td>
<td>30.7±1.9</td>
<td>2+5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>98.2±0.2</td>
<td>-81.8±1.5</td>
<td>0.22±0.10</td>
<td>148.1±4.2</td>
<td>130.1±9.2</td>
<td>16.4±1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb2{S2P(O-C6H11)2}4]2+</td>
<td>98.1±0.2</td>
<td>-63.1±1.0</td>
<td>0.91±0.03</td>
<td>158.5±1.4</td>
<td>100.9±2.6</td>
<td>35.0±1.0</td>
<td>2+4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>94.5±0.1</td>
<td>309; 57</td>
<td>+61.3±0.8</td>
<td>155.8±0.8</td>
<td>75.7±3.2</td>
<td>52.1±1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb{S2P(O-C7H14)2}2]n</td>
<td>94.4±1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2+4</td>
</tr>
<tr>
<td>[Pb{S2P(O-C8H14)2}2]n</td>
<td>99.0±0.1</td>
<td>-69.4±1.1</td>
<td>0.59±0.05</td>
<td>154.1±1.9</td>
<td>113.3±3.8</td>
<td>29.7±1.1</td>
<td>2+5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>98.7±0.1</td>
<td>-68.8±1.2</td>
<td>0.65±0.05</td>
<td>155.4±1.8</td>
<td>110.9±3.7</td>
<td>29.9±1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb{S2P(O-C8H15)2}2]n</td>
<td>99.6±0.2</td>
<td>-59.0±1.1</td>
<td>0.83±0.05</td>
<td>153.5±1.7</td>
<td>104.8±3.3</td>
<td>40.7±1.1</td>
<td>2+4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95.6±0.2</td>
<td>-64.4±1.2</td>
<td>0.88±0.04</td>
<td>156.1±1.7</td>
<td>99.6±3.2</td>
<td>31.2±1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean***</td>
<td>97.9±0.1</td>
<td>-67.8±0.3</td>
<td>0.64±0.02</td>
<td>152.6±0.8</td>
<td>111.0±1.8</td>
<td>30.1±0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* zJ(31P, 207Pb)-coupling
** Too broad resonance lines to make unambiguous CSA simulations.
*** The terminal ligand of the di-iso-butyldithiophosphate complex was omitted due to its different sign of δaniso (unusually small S-P-S angle, see later).

Table 3 shows the known X-ray structural data for the lead complexes in this study. The ligands are tridentate, combining terminal and bridging functions, the only exception being the purely terminal ligand in the di-iso-butyldithiophosphate, and to some extent the mononuclear diethyldithiophosphate ligands which only have weak van der Waals-like bonds to the neighboring molecules.
Correlations between CSA and structural parameters

Figure 50 shows a stick diagram of the mean $^{31}$P chemical shift tensor principal values, $\delta_{11}$, $\delta_{22}$ and $\delta_{33}$, for the different types of dialkyldithiophosphates in this study, revealing the general shape of the tensors. It can be seen that $\delta_{22}$ is the component responsible for the change in sign of $\delta_{\text{aniso}}$ as it varies from being close to $\delta_{11}$ for the ligands in the potassium dithiophosphates to being close to $\delta_{33}$ for the terminal ligands of zinc(II) and nickel(II) dialkyldithiophosphates.

![Stick diagram showing chemical shift tensors for different types of dialkyldithiophosphate ligands.](image)

The potassium dithiophosphate salts have the largest span of the chemical shift tensor, which is almost axially symmetric. The shapes of the tensors are similar for the terminal ligands in the different complexes and have positive $\delta_{\text{aniso}}$ ($\delta_{22}$ closer to $\delta_{33}$ than to $\delta_{11}$). The bridging ligands in the zinc(II) dithiophosphates have a general shape of the CST that is a mirror image of the CST of the terminal ligands. The lead(II) dithiophosphates have a CST that is almost identical to the one for the tetranuclear zinc(II) dithiophosphates, and have $\eta$ close to 1.

In order to see which structural parameter is responsible for the changes of the $^{31}$P CST, it is appropriate to investigate the relationship between the principal values of the chemical shift tensor and bond angles or bond lengths within the molecules.
Figure 51 shows the results of such investigations for the nickel(II) and zinc(II) dialkyldithiophosphates. The CST parameters of the dithiophosphate compounds with known crystal structure were plotted against different structural parameters, such as P-O and P-S bond lengths and O-P-O and S-P-S bond angles.

![CST parameters vs. structural parameters](image)

Figure 51 $^{31}$P chemical shift tensor principal values versus: S-P (a) and O-P (b) bond lengths, S-P-S (c) and O-P-O (d) bond angles obtained from known X-ray diffraction structures for nickel(II) and zinc(II) dialkyldithiophosphate complexes. Solid lines are guides to the eye.

Ab-initio quantum mechanical calculations of the $^{31}$P chemical shift tensors (CST) have been performed on an [O$_2$PS$_2$]$^-$ model fragment. Table 10 shows the results of the calculations when the P-O and P-S bond lengths have been varied.

73
Table 10  Calculated $^{31}$P chemical shielding tensor parameters as a function of P-O and P-S bond lengths in the model compound [(CH$_3$O)$_2$PS$_2$]$^-$.  

<table>
<thead>
<tr>
<th>P-O bond length* (Å)</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{aniso}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.61</td>
<td>220.3</td>
<td>129.0</td>
<td>164.0</td>
<td>368.0</td>
<td>239.0</td>
<td>0.707</td>
<td>-147.7</td>
<td>0.237</td>
</tr>
<tr>
<td>1.65</td>
<td>207.7</td>
<td>109.0</td>
<td>145.9</td>
<td>368.2</td>
<td>259.2</td>
<td>0.715</td>
<td>-160.5</td>
<td>0.230</td>
</tr>
<tr>
<td>1.66</td>
<td>204.5</td>
<td>104.1</td>
<td>141.3</td>
<td>368.2</td>
<td>264.1</td>
<td>0.718</td>
<td>-163.7</td>
<td>0.227</td>
</tr>
<tr>
<td>1.67</td>
<td>201.3</td>
<td>99.2</td>
<td>136.6</td>
<td>368.2</td>
<td>269.0</td>
<td>0.722</td>
<td>-166.9</td>
<td>0.224</td>
</tr>
<tr>
<td>1.71</td>
<td>188.5</td>
<td>79.9</td>
<td>117.6</td>
<td>367.9</td>
<td>288.0</td>
<td>0.738</td>
<td>-179.4</td>
<td>0.210</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P-S bond length* (Å)</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{aniso}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.95</td>
<td>226.0</td>
<td>127.7</td>
<td>165.5</td>
<td>384.8</td>
<td>257.1</td>
<td>0.706</td>
<td>-158.8</td>
<td>0.238</td>
</tr>
<tr>
<td>1.99</td>
<td>208.9</td>
<td>109.0</td>
<td>146.2</td>
<td>371.5</td>
<td>262.5</td>
<td>0.717</td>
<td>-162.6</td>
<td>0.229</td>
</tr>
<tr>
<td>2.00</td>
<td>204.5</td>
<td>104.1</td>
<td>141.3</td>
<td>368.2</td>
<td>264.1</td>
<td>0.718</td>
<td>-163.7</td>
<td>0.227</td>
</tr>
<tr>
<td>2.01</td>
<td>200.0</td>
<td>99.11</td>
<td>136.2</td>
<td>364.8</td>
<td>265.7</td>
<td>0.720</td>
<td>-164.8</td>
<td>0.225</td>
</tr>
<tr>
<td>2.05</td>
<td>181.8</td>
<td>78.71</td>
<td>115.5</td>
<td>351.3</td>
<td>272.6</td>
<td>0.730</td>
<td>-169.5</td>
<td>0.217</td>
</tr>
</tbody>
</table>

* Bond lengths in the B3LYP optimized structures

It can be seen that for both the P-O and P-S bond lengths the isotropic shielding increases when the bond length increases. $\sigma_{33}$ is not much affected by the changes in bond lengths, while changes in $\sigma_{11}$ and $\sigma_{22}$ follow each other. The changes do not lead to any change in sign of $\delta_{aniso}$. Figures 51a and 51b (experimental CST data) do not reveal any correlation between bond lengths and CST parameters.

The results of changes in the O-P-O bond angle are displayed in Table 11. $\sigma_{iso}$ passes through a maximum at ca. 100°. $\sigma_{11}$ reaches a maximum at ca. 96°, while $\sigma_{22}$ reaches its minimum at this angle. $\sigma_{33}$ decreases as the angle increases. $\delta_{aniso}$ does not change sign with changing of the O-P-O angle. Figure 51d shows small tendencies of changes in the CST principal values with varying O-P-O bond angle.
angle, but this is an effect of the simultaneous change in both O-P-O and S-P-S angles in the real systems.

Table 11. Calculated \(^{31}\)P chemical shielding tensor parameters as a function of O-P-O bond angle in the model compound \([(\text{CH}_3\text{O})_2\text{PS}_2]^−\).

<table>
<thead>
<tr>
<th>O-P-O bond angle*</th>
<th>(\sigma_{iso}) (ppm)</th>
<th>(\sigma_{11}) (ppm)</th>
<th>(\sigma_{22}) (ppm)</th>
<th>(\sigma_{33}) (ppm)</th>
<th>(\Omega) (ppm)</th>
<th>(\kappa)</th>
<th>(\delta_{aniso}) (ppm)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.6°</td>
<td>202.7</td>
<td>82.4</td>
<td>171.1</td>
<td>354.7</td>
<td>272.3</td>
<td>0.348</td>
<td>-152.0</td>
<td>0.584</td>
</tr>
<tr>
<td>104.5°</td>
<td>203.8</td>
<td>101.2</td>
<td>152.9</td>
<td>357.2</td>
<td>256.0</td>
<td>0.596</td>
<td>-153.4</td>
<td>0.337</td>
</tr>
<tr>
<td>100.3°</td>
<td>204.1</td>
<td>116.9</td>
<td>135.3</td>
<td>360.0</td>
<td>243.1</td>
<td>0.849</td>
<td>-155.9</td>
<td>0.118</td>
</tr>
<tr>
<td>96.1°</td>
<td>203.9</td>
<td>118.5</td>
<td>129.7</td>
<td>363.4</td>
<td>244.9</td>
<td>0.909</td>
<td>-159.5</td>
<td>0.070</td>
</tr>
<tr>
<td>91.8°</td>
<td>203.4</td>
<td>102.7</td>
<td>139.8</td>
<td>367.8</td>
<td>265.1</td>
<td>0.720</td>
<td>-164.4</td>
<td>0.226</td>
</tr>
<tr>
<td>87.4°</td>
<td>202.6</td>
<td>86.1</td>
<td>148.1</td>
<td>373.6</td>
<td>287.5</td>
<td>0.569</td>
<td>-171.0</td>
<td>0.363</td>
</tr>
</tbody>
</table>

* Bond angles in the B3LYP optimized structures

Table 12 shows the dependence of the \(^{31}\)P chemical shielding parameters on the S-P-S angle. As the bond angle increases, \(\sigma_{iso}\) does not change considerably, while \(\sigma_{11}\) and \(\sigma_{33}\) also increases. \(\sigma_{22}\) decreases with an increase in the S-P-S angle, see Figure 52.

Table 12. Calculated \(^{31}\)P chemical shielding tensors (ppm) as a function of S-P-S bond angle in the model compound \([(\text{CH}_3\text{O})_2\text{PS}_2]^−\).

<table>
<thead>
<tr>
<th>S-P-S bond angle*</th>
<th>(\sigma_{iso}) (ppm)</th>
<th>(\sigma_{11}) (ppm)</th>
<th>(\sigma_{22}) (ppm)</th>
<th>(\sigma_{33}) (ppm)</th>
<th>(\Omega) (ppm)</th>
<th>(\kappa)</th>
<th>(\delta_{aniso}) (ppm)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125°</td>
<td>202.8</td>
<td>102.0</td>
<td>126.4</td>
<td>380.0</td>
<td>278.0</td>
<td>0.824</td>
<td>-177.2</td>
<td>0.138</td>
</tr>
<tr>
<td>120°</td>
<td>203.4</td>
<td>102.6</td>
<td>139.3</td>
<td>368.3</td>
<td>265.7</td>
<td>0.724</td>
<td>-164.9</td>
<td>0.223</td>
</tr>
<tr>
<td>115°</td>
<td>203.6</td>
<td>102.9</td>
<td>151.7</td>
<td>356.1</td>
<td>253.2</td>
<td>0.615</td>
<td>-152.5</td>
<td>0.320</td>
</tr>
<tr>
<td>98°</td>
<td>201.8</td>
<td>95.9</td>
<td>198.5</td>
<td>310.9</td>
<td>215.0</td>
<td>0.046</td>
<td>-109.1</td>
<td>0.940</td>
</tr>
<tr>
<td>95°</td>
<td>201.2</td>
<td>91.9</td>
<td>209.5</td>
<td>302.3</td>
<td>210.4</td>
<td>-0.118</td>
<td>109.3</td>
<td>0.849</td>
</tr>
<tr>
<td>93°</td>
<td>200.9</td>
<td>88.3</td>
<td>217.8</td>
<td>296.5</td>
<td>208.2</td>
<td>-0.244</td>
<td>112.6</td>
<td>0.699</td>
</tr>
</tbody>
</table>

* Bond angles in the B3LYP optimized structures
Figure 51c shows that the experimental data follow the same trend of increasing $\delta_{22}$ when the S-P-S angle increases. $\delta_{11}$ and $\delta_{33}$ also seem to follow the trends given by ab-initio calculations, although less pronounced.

It can be seen that for the changes in the S-P-S angle $\delta_{\text{aniso}}$ changes sign and becomes positive at small angles ($<95^\circ$) and negative at larger angles. X-ray data for the dithiophosphate complexes show that the S-P-S angles in the terminal ligands are smaller than in the bridging, which leads to a positive sign of $\delta_{\text{aniso}}$. Note that the bridging ligand in the zinc(II) diethylidithiophosphate complex, for which $\delta_{\text{aniso}} > 0$ has an S-P-S angle of the same size as the angles in the terminal ligands of the nickel and zinc complexes.

A similar study on the lead(II) dialkyldithiophosphates also shows correlations between the S-P-S angle and the CST principal values, see Figure 53.
Figure 53. $^{31}$P chemical shift tensor principal values versus S-P-S bond angles obtained from NMR data and known X-ray diffraction structures for dialkyldithiophosphate lead(II) complexes. Solid lines are guides to the eye.

As both $\delta_{22}$ and $\delta_{33}$ changes simultaneously, although with different slopes, the isotropic chemical shift is almost conserved, decreasing slightly for smaller S-P-S angles.

The slopes of hypothetical lines between the data points of $\delta_{22}$ versus the S-P-S angle are different for the zinc(II) dithiophosphates, as compared to the lead(II) dithiophosphates, see Figure 54. $\delta_{22}$ is more sensitive to changes in the S-P-S angle in the lead(II) complexes, as compared to the zinc(II) complexes.
Ab-initio calculations of the chemical shift tensors were also performed on a few nickel(II) and zinc(II) dialkyldithiophosphates with known crystal structures. The calculations were performed with two different basis sets on P, S and O and the results were compared with the experimental NMR data. Tables 13 and 14 show the results of calculations of the CSTs for the terminal and bridging ligands, respectively. The isotropic chemical shifts and the CST parameters can not be compared directly as the calculated values are relative to the bare phosphorus nucleus while the experimental values are compared to the phosphorus nucleus in 85% H₃PO₄, as external reference. However, the CST parameters $\Omega$, $\kappa$, $\delta_{\text{aniso}}$, and $\eta$ are relative measures and independent of the reference scale used, and can thus be directly compared with each other.

Comparison between the experimental and the theoretical values of the CST parameters is not perfect, but the results of ab-initio quantum mechanical calculations follow the general experimental trends that the terminal ligands (with smaller S-P-S angles) have positive $\delta_{\text{aniso}}$ while the bridging ligands (with larger S-P-S angles) have negative $\delta_{\text{aniso}}$. Terminal ligands have smaller span than the
bridging ligands. The data for the bridging ligand of the zinc(II) diethyldithiophosphate compound deviate a lot because the calculations were performed on a binuclear fragment with optimized geometry similar to the one for the di-\textit{iso}-propyldithiophosphate, but the structure revealed by single-crystal X-ray diffraction is in fact an infinite polymeric chain, in which the bridging ligand have a different geometry.
Table 13. Calculated $^{31}$P chemical shielding tensor parameters for terminal ligands in nickel(II) and zinc(II) dialkyldithiophosphate complexes, with data in parentheses from experimental results.

<table>
<thead>
<tr>
<th>S-P-S Bond angle</th>
<th>$\sigma_{nn}$ (ppm)</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{\text{aniso}}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn$_2$(S$_2$P(O-(i)-C$_3$H$_7$)$_2$)$_4$]</td>
<td>109.5°</td>
<td>225.4</td>
<td>168.9</td>
<td>249.9</td>
<td>257.3</td>
<td>88.4</td>
<td>-0.831</td>
<td>56.5</td>
</tr>
<tr>
<td>[Zn$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
<td>110.35°</td>
<td>227.3</td>
<td>178.2</td>
<td>249.0</td>
<td>254.8</td>
<td>76.6</td>
<td>-0.850</td>
<td>49.1</td>
</tr>
<tr>
<td>[Ni$_2$(S$_2$P(O-(i)-C$_3$H$_7$)$_2$)$_4$]</td>
<td>104.43°</td>
<td>229.9</td>
<td>172.8</td>
<td>256.4</td>
<td>260.6</td>
<td>87.8</td>
<td>-0.905</td>
<td>57.1</td>
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<td>[Ni$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
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<td>181.6</td>
<td>247.5</td>
<td>269.8</td>
<td>88.2</td>
<td>-0.493</td>
<td>51.4</td>
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</table>

<table>
<thead>
<tr>
<th>S-P-S Bond angle</th>
<th>$\sigma_{nn}$ (ppm)</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{\text{aniso}}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni$_2$(S$_2$P(O-(i)-C$_3$H$_7$)$_2$)$_4$]</td>
<td>105.1°</td>
<td>153.3</td>
<td>82.4</td>
<td>187.7</td>
<td>189.8</td>
<td>107.4</td>
<td>-0.961</td>
<td>70.9</td>
</tr>
<tr>
<td>[Zn$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
<td>110.3°</td>
<td>156.6</td>
<td>95.7</td>
<td>181.6</td>
<td>192.4</td>
<td>96.7</td>
<td>-0.776</td>
<td>60.9</td>
</tr>
<tr>
<td>[Ni$_2$(S$_2$P(O-(i)-C$_3$H$_7$)$_2$)$_4$]</td>
<td>104.5°</td>
<td>159.2</td>
<td>87.5</td>
<td>192.0</td>
<td>198.0</td>
<td>110.5</td>
<td>-0.890</td>
<td>71.7</td>
</tr>
<tr>
<td>[Ni$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
<td>105.1°</td>
<td>161.5</td>
<td>100.6</td>
<td>176.2</td>
<td>207.8</td>
<td>107.2</td>
<td>-0.411</td>
<td>60.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S-P-S Bond angle</th>
<th>$\sigma_{nn}$ (ppm)</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{\text{aniso}}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
<td>105.1°</td>
<td>172.2</td>
<td>102.2</td>
<td>181.1</td>
<td>233.3</td>
<td>131.1</td>
<td>-0.204</td>
<td>70.0</td>
</tr>
</tbody>
</table>

$^1$ Mean of bond angles in the B3LYP optimized structures

6-31G** basis on P, S, and O

6-311+G(2d) basis on P, S, and O

6-311+G(2d) basis on P, S, and O and DZ basis on Ni
Table 14. Calculated $^{31}$P chemical shielding tensor parameters for bridging ligands in dialkyldithiophosphate zinc(II) complexes, with data in parentheses from experimental results.

<table>
<thead>
<tr>
<th>6-31G**</th>
<th>6-311+G(2d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S-P-S bond angle</td>
</tr>
<tr>
<td>[Zn$_2$(S$_2$P(O-i-C$_3$H$_7$)$_2$)$_4$]</td>
<td>113.9°</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Zn$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn($S_2$P(OC$_2$H$_5$)$_2$)$_2$]$_n$</td>
<td>117.4°</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn$_4$(S$_2$P(O-i-C$_3$H$_7$)$_2$)$_4$]</td>
<td>121.4°</td>
</tr>
<tr>
<td>[Zn$_4$(S$_2$P(OC$_2$H$_5$)$_2$)$_4$]</td>
<td>117.4°</td>
</tr>
</tbody>
</table>

$^1$ Mean of bond angles in the B3LYP optimized structures

The addition of a metal atom to the O$_2$PS$_2$-tetrahedron will most likely distort the CST from its ideal position in the undistorted tetrahedron. The ab-initio calculations of the CSTs in the metal complexes give the eigenvectors of the principal axes for the given molecular geometry ($\sigma_{iso}$). Assuming that the distortions of the tensor by the presence of the metal atom are small the same molecular coordinates can be used to determine the eigenvectors of the principal axes for the tensor with the same orientation as in the model fragment [(CH$_3$O)$_2$PS]$.^+$ ($\sigma_{undist}$). Table 15 shows the results of such calculations, given as $\Delta_{nn}$, the number of degrees each principal axis is rotated from the position in the model fragment. The deviation from the tetrahedral geometry has also been calculated, given as $\phi$, the number of degrees the vector connecting the two
The deviations in the tensor components due to the binding of a metal atom are reasonably small for the terminal ligands, but for the bridging ligands the deviations are too large to be relied upon. The higher flexibility of the eight-membered ring structure can cause large distortions in the geometry and electronic environment around the $^{31}$P sites in comparison to the more rigid four-membered ring in the terminal parts of the molecule.

Table 15. Deviations between geometries of the undistorted $^{31}$P chemical shift tensor (in the model [(CH$_3$O)$_2$PS$_2]^-$ fragment) and the tensor distorted due to bonding to metal atoms in calculated nickel(II) and zinc(II) dithiophosphate complexes ($^\circ$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Terminal ligands</th>
<th>Bridging ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta_{11}$ ($^\circ$)</td>
<td>$\Delta_{22}$ ($^\circ$)</td>
</tr>
<tr>
<td></td>
<td>$\Delta_{11}$ ($^\circ$)</td>
<td>$\Delta_{22}$ ($^\circ$)</td>
</tr>
<tr>
<td>[Ni(S$_2$P(OC$_2$H$_5$)$_2$)$_2$]</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>6-31G**</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>[Ni(S$_2$P(O-i-C$_3$H$_7$)$_2$)$_2$]</td>
<td>10.4$^a$</td>
<td>10.4$^a$</td>
</tr>
<tr>
<td>6-311+G(2d)</td>
<td>10.5$^a$</td>
<td>10.5$^a$</td>
</tr>
<tr>
<td>[Zn$_2$(S$_2$P(O-i-C$_3$H$_7$)$_2$)$_2$]</td>
<td>14.8$^a$</td>
<td>14.1$^a$</td>
</tr>
<tr>
<td>6-31G**</td>
<td>4.4$^a$</td>
<td>3.4$^a$</td>
</tr>
<tr>
<td>[Zn$_2$(S$_2$P(O-i-C$_3$H$_7$)$_2$)$_2$]</td>
<td>41.8$^a$</td>
<td>41.6$^a$</td>
</tr>
<tr>
<td>6-311+G(2d)</td>
<td>24.8$^a$</td>
<td>24.6$^a$</td>
</tr>
<tr>
<td>[Zn$_4$S(S$_2$P(OC$_2$H$_5$)$_2$)$_6$]</td>
<td>10.7</td>
<td>20.5</td>
</tr>
<tr>
<td>6-31G**</td>
<td>11.2</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>9.8</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>19.2</td>
</tr>
</tbody>
</table>

$^a$ Can be disregarded due to almost axially symmetric $^{31}$P CSTs.

$^1 \Delta_{nn} = \arccos \left( \frac{|\mathbf{\sigma}_{nn}^{\text{dist}} \cdot \mathbf{\sigma}_{nn}^{\text{undist}}|}{|\mathbf{\sigma}_{nn}^{\text{dist}}| \cdot |\mathbf{\sigma}_{nn}^{\text{undist}}|} \right)$

$^2 \phi = \arccos \left( \frac{|\mathbf{O} \cdot \mathbf{S}|}{|\mathbf{O}| \cdot |\mathbf{S}|} \right)$
Figure 55 shows single-pulse $^{207}$Pb NMR spectra of three different lead(II) dialkyldithiophosphate complexes.

![NMR spectra of lead(II) dialkyldithiophosphates](image)

The span for these complexes is more than 3000 ppm. The large chemical shift anisotropy of the lead atoms leads to experimental difficulties. The edges of the spectral pattern will not be as efficiently excited as the central region, leading to distortions in the intensities of the spinning sidebands, which leads to unreliable simulations of chemical shift parameters.

CSA simulations using spinning sideband intensities were performed for different combinations of spinning sidebands in the central region of the $^{207}$Pb NMR spectra, where the carrier frequency was set, stepping from $-7 / +7$, to $-7 / +6$, ..., $-6 / +7$, $-6 / +6$, ..., etc. to find the “stable” region for the CSA parameters. The program displays $\chi^2$-plots for two different confidence intervals (95.7%, dashed lines and 68.4%, solid lines). Figure 56 shows the $\chi^2$-plots for three of the
simulations with different spinning sideband intervals. The plots of the unreliable sideband regions drift towards the computational limit of the program ($\delta_{\text{aniso}} = -1600$ ppm), while the reliable ones are well resolved (highlighted ellipses in Figure 56). The reliable range for the simulations was found to be in the region from +5 to –5 sidebands when the carrier frequency was set between the central band and the +1 spinning sideband.

![Figure 56. $\chi^2$-plots for $^{207}$Pb CSA parameters $\delta_{\text{aniso}}$ and $\eta$ (Pb(II) di-iso-butyldithiophosphate, 12 kHz). 95.4% (dashed lines) and 68.3% (solid lines) joint confidence limits, respectively. Spinning sideband intervals were –5,..., +4 (thick lines) and –6,..., +3 (small features) and 0,..., +4 (large features), respectively (thin lines).](image)

Table 16 shows the chemical shift data for the three dialkyldithiophosphate lead(II) complexes studied. The CSA for the diethylidithiophosphate complex could not be simulated. The reason is that the value of $\delta_{\text{aniso}}$ is outside the current computational range of the program. However, a rough estimate of the principal values from the span of the spectrum indicate that $\delta_{\text{aniso}} \approx 1900$ ppm, which is outside the computational region.
Table 16  $^{207}$Pb chemical shift anisotropy parameters obtained at 12 kHz spinning frequency

<table>
<thead>
<tr>
<th>Complex (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\delta_{aniso}$ (ppm)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pb}{S_2\text{P(OCH}_3\text{)}<em>2}]</em>{2}$</td>
<td>-1040</td>
<td>1900*</td>
<td>0.2*</td>
</tr>
<tr>
<td>$[\text{Pb}{S_2\text{P(OH)}<em>2}]</em>{n}$</td>
<td>-857</td>
<td>-1178</td>
<td>0.49</td>
</tr>
<tr>
<td>$[\text{Pb}_2{S\text{P(O-i-C}_4\text{H}_9)}_2}_4$</td>
<td>-650</td>
<td>-1367</td>
<td>0.44</td>
</tr>
</tbody>
</table>

* Estimated from the span of the spinning sideband pattern in the spectrum
SURFACE COMPLEXES

ZnS

Table 17 shows $^{31}$P isotropic chemical shifts of the dithiophosphates adsorbed at the surface of synthetic sphalerite (ZnS).

**Table 17. $^{31}$P chemical shifts of sodium dialkyldithiophosphates adsorbed at the surface of synthetic sphalerite (ZnS).**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>line width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-diethyldithiophosphate</td>
<td>104.6</td>
<td>900</td>
</tr>
<tr>
<td>ZnS-di-$n$-propyldithiophosphate</td>
<td>102.5</td>
<td>550</td>
</tr>
<tr>
<td>ZnS-di-$i$-propyldithiophosphate*</td>
<td>97.6</td>
<td>560</td>
</tr>
<tr>
<td>ZnS-di-$n$-butyldithiophosphate</td>
<td>102.8</td>
<td>520</td>
</tr>
<tr>
<td>ZnS-di-$i$-butyldithiophosphate</td>
<td>102.4</td>
<td>620</td>
</tr>
<tr>
<td>ZnS-di-$s$-butyldithiophosphate</td>
<td>97.2</td>
<td>630</td>
</tr>
<tr>
<td>ZnS-di-$i$-amyldithiophosphate</td>
<td>102.9</td>
<td>550</td>
</tr>
<tr>
<td>ZnS-di-cyclo-hexyldithiophosphate</td>
<td>97.5</td>
<td>740</td>
</tr>
</tbody>
</table>

*Potassium

In order to determine the type of sorption that has occurred on the surface it is important to compare $^{31}$P chemical shifts of the surface species with the chemical shifts of the ionic and polycrystalline dithiophosphates. Comparison with the chemical shifts of the corresponding ionic salts (Table 5) shows that the surface complexation leads to smaller chemical shifts. The chemical shifts are in the same range as the covalent ligands of the polycrystalline zinc complexes (Table 7 and Table 8), suggesting covalent bonding of the ligand to the surface. The surface complexation is also characterized by a broadening of the $^{31}$P resonance lines in the NMR spectra. This broadening is due to an effect of the surface inhomogeneity leading to a spread of chemical shifts.

Figure 57 shows $^{31}$P CP/MAS NMR spectra of the surface complex, the ionic salt and the polycrystalline zinc(II) di-$iso$-propyldithiophosphate complexes.
Figure 57. $^{31}$P CP/MAS NMR spectra of di-iso-propyl dithiophosphate: a) adsorbed on the surface of synthetic sphalerite, b) binuclear zinc(II) complex, c) tetranuclear zinc(II) complex and (d) sodium salt.

The $^{31}$P chemical shift of the surface species overlaps with the chemical shifts of the bridging ligands in the binuclear and tetranuclear zinc complexes, suggesting a bridging coordination of the ligand to the surface of the synthetic sphalerite. The same good correlation between the chemical shift of the surface complex and the bridging ligands of the polycrystalline zinc complexes can also be seen for the zinc(II) di-$n$-propyl, di-$n$-butyl and di-iso-amyldithiophosphate complexes.

Figure 58 shows the overlapped spectra of the surface complex, the ionic salt and the polycrystalline zinc di-cyclo-hexyldithiophosphate complexes.

Figure 58. $^{31}$P CP/MAS NMR spectra of di-cyclo-hexyldithiophosphate: a) adsorbed on the surface of synthetic sphalerite, b) binuclear zinc(II) ($T > 316$ K conformer) and c) sodium salt.
The chemical shift of the surface species for this ligand as well as for di-iso-butyl and di-sec-butyl dithiophosphates is in the range between the chemical shifts of the terminal and the bridging ligands in the corresponding binuclear zinc complexes. However, a bridging coordination seems more likely as this requires only one free binding site on the zinc atom (corresponding to a coordination number of three), instead of two (corresponding to a coordination number of two) which would be the case for terminal coordination to occur.

Figure 59 shows the overlapped spectra of the surface complex, the ionic salt and the polycrystalline zinc diethylidithiophosphate complexes.

Figure 59. $^{31}$P CP/MAS NMR spectra of diethylidithiophosphate: a) adsorbed on the surface of synthetic sphalerite, b) polymeric zinc(II) complex, c) tetranuclear zinc(II) complex and d) sodium salt.

The chemical shift of the surface complex seems to have a larger ionic character than the other ligands and is in the range between the ionic salt and the bridging ligands of the polycrystalline chemical shifts.

In the binuclear zinc cyclo-hexyl complex the Zn-Zn distance is 4.170 Å while it is only 3.697 Å in the tetranuclear Zn$_4$S diethylidithiophosphate. The Zn-Zn distance in sphalerite is 3.824 Å, which makes a bridging coordination of the dithiophosphate ligands possible.

The spectra of dithiophosphate ligands adsorbed on the surface of synthetic sphalerite also showed traces of oxidation and hydrolysis products, see Figure 60.
Figure 60. $^{31}$P CP/MAS NMR spectra of di-s-butyldithiophosphate adsorbed on the surface of synthetic sphalerite. ssb = spinning sideband, ds = disulfide, ph = phosphate.

The disulfide has a chemical shift at ca. 75 ppm [42] and phosphate species can be found close to 0 ppm [43].

**PbS**

Figure 61 shows $^{31}$P CP/MAS NMR spectra of different surface adsorbed compounds on PbS. The spectra show a broad resonance at ca. 95 ppm. The spectra of freshly adsorbed diethyl- and di-iso-butyldithiophosphates, and possibly also di-n-butyldithiophosphate, show traces of hydrolysis products at ca. 45 ppm corresponding to monothiophosphates [44] and the di-iso-butyldithiophosphate spectrum also shows traces of orthophosphates at ca. 0 ppm. The spectra of the aged samples show that monothiophosphates and/or orthophosphates have formed except from the di-cyclo-hexyldithiophosphate ligand. It is interesting to note that no traces of disulfide can be found in the spectra ($\delta_{iso} \approx 70$ ppm).
Table 18 shows the isotropic chemical shifts of the dithiophosphates adsorbed at the surface of synthetic galena (PbS), one day and three months after the adsorption, respectively.

Comparison with the chemical shifts of the corresponding potassium salts (Table 5) shows that the surface complexation leads to more shielded chemical shifts. The chemical shifts are in the same range as the covalent ligands of the polycrystalline lead complexes (Table 9), suggesting covalent bonding of the ligand to the surface. The surface complexation also leads to a broadening of the resonance line due to the inhomogeneity of the surface.
Table 18. Chemical shifts of potassium dialkyldithiophosphates adsorbed at the surface of synthetic galena (PbS).

<table>
<thead>
<tr>
<th>Surface complex</th>
<th>Fresh sample</th>
<th>Aged sample</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ line</td>
<td>δ line</td>
<td></td>
</tr>
<tr>
<td></td>
<td>width</td>
<td>width</td>
<td></td>
</tr>
<tr>
<td>PbS-di-ethyl dithiophosphate</td>
<td>94.1</td>
<td>95.8</td>
<td>Surface complexation</td>
</tr>
<tr>
<td></td>
<td>46.5</td>
<td>48.6</td>
<td>Monothiophosphate [PSO₃]</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-0.6</td>
<td>Orthophosphate [PO₄]</td>
</tr>
<tr>
<td>PbS-di-n-propyl dithiophosphate</td>
<td>95.5</td>
<td>96.2</td>
<td>Surface complexation</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>434</td>
<td>Monothiophosphate [PSO₃]</td>
</tr>
<tr>
<td></td>
<td>92.8</td>
<td>92.8</td>
<td>Orthophosphate [PO₄]</td>
</tr>
<tr>
<td>PbS-di-n-butyldithiophosphate</td>
<td>96.8</td>
<td>97.0</td>
<td>Bulk precipitate</td>
</tr>
<tr>
<td></td>
<td>381</td>
<td>224</td>
<td>Surface complexation</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>1040</td>
<td>Monothiophosphate [PSO₃]</td>
</tr>
<tr>
<td></td>
<td>47.7</td>
<td>47.4</td>
<td>Orthophosphate [PO₄]</td>
</tr>
<tr>
<td>PbS-di-cyclo-hexyl dithiophosphate</td>
<td>96.5</td>
<td>95.8</td>
<td>Bulk precipitate</td>
</tr>
<tr>
<td></td>
<td>95.8</td>
<td>95.5</td>
<td>Surface complexation</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>598</td>
<td></td>
</tr>
<tr>
<td></td>
<td>451</td>
<td>515</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.3</td>
<td>94.3</td>
<td></td>
</tr>
</tbody>
</table>
The isotropic part of the NMR spectra are shown in Figure 62 overlapped with the isotropic chemical shifts of the corresponding polycrystalline lead(II) dialkyldithiophosphate complexes.

![Figure 62. $^{31}$P CP/MAS NMR spectra of isotropic chemical shifts for diethyl a), di-n-propyl b), di-iso-propyl c), di-n-butyl d), di-iso-butyl e) and di-cyclo-hexyl f) dithiophosphates adsorbed on the surface of synthetic galena. Corresponding polycrystalline lead(II) dialkyldithiophosphate complexes are inserted.](image-url)
The general situation is that the $^{31}$P resonance lines of the surface complexes are broader and these sites are more shielded than the phosphorus sites in the polycrystalline dialkyldithiophosphate lead(II) complexes. The spectrum of the di-iso-propyldithiophosphate ligand also shows presence of the precipitated di-iso-propyldithiophosphate lead(II) complex, as a sharper resonance line at the same chemical shift as for the polycrystalline complex is present in the spectrum. The spectra of the di-n-butyl and the di-iso-butyldithiophosphates have a sharp feature in the middle of the broad resonance line. The majority of the polycrystalline lead samples in this study have ligands with combined structural functions, with a tridentate coordination both terminal and bridging. However, the general trend is that within a molecule the larger the terminal character of the ligand the more shielded the isotropic chemical shift is, due to a slightly smaller S-P-S angle, see Table 3. This trend makes it reasonable to suggest a terminal coordination of the dithiophosphates to the surface of synthetic galena.

A terminal coordination requires an increase in the coordination of lead by two. The larger radius and the larger coordination number (six) of lead in galena makes it possible to add two bonds to the same surface lead atom.

The spectra of the same samples after three months of storing, without any efforts to exclude air, are shown in the right part of Figure 60.

In the spectrum of diethyldithiophosphate adsorbed on PbS any dithiophosphate is no longer present in the sample since the resonance line at 96 ppm is absent. Small traces of monothiophosphate can be seen at ca. 50 ppm and a large amount of orthophosphate can be detected at 0 ppm. The diethyldithiophosphate compound is the least hydrophobic of the dithiophosphates in this study and thus should be most prone to hydrolysis reactions.

The other ligands are still present as dithiophosphates adsorbed on the surface of galena. However, the amount of hydrolysis products have increased after the storage. The only exception is the di-cyclo-hexyldithiophosphate, which shows no signs of hydrolysis, possibly because of the high hydrophobicity due to the bulky cyclo-hexyl rings. The polycrystalline di-cyclo-hexyldithiophosphate lead(II)
complex has instead formed as a precipitate (narrow resonance lines at 99 and 96 ppm, corresponding to the polymeric lead(II) di-cyclo-hexyldithiophosphate, see Table 9). The amount of precipitated lead(II) di-iso-propylidithiophosphate has also increased during the storing time of three months at ambient conditions.
CONCLUSIONS

Sodium and potassium dialkyldithiophosphates with eight different alkyl chains (R=ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, iso-amyl and cyclo-hexyl) were investigated with $^{31}$P and $^{13}$C CP/MAS NMR, both as ligands of polycrystalline nickel(II), zinc(II) and lead(II) dithiophosphate complexes and as surface adsorbed on the surface of synthetic ZnS and PbS. Some of the polycrystalline lead(II) dithiophosphates were further investigated with solid-state $^{207}$Pb NMR.

The $^{31}$P and $^{207}$Pb chemical shift anisotropy parameters, $\delta_{\text{aniso}}$ and $\eta$, were estimated from the spinning sideband patterns in the NMR spectra. By comparing $^{31}$P isotropic chemical shifts and $^{31}$P CSA parameters of polycrystalline nickel(II), zinc(II) and lead(II) complexes, with different types of ligands, i. e. bidentate terminal, bridging or tridentate, it was possible to assign the most shielded phosphorus sites to the terminal ligands.

CSA analysis of the nickel(II), zinc(II) and lead(II) dithiophosphates revealed a linear correlation between the chemical shift tensor principal value $\delta_{22}$ and the S-P-S angle in the ligands, leading to $\delta_{\text{aniso}} > 0$ for small S-P-S angles. This correlation was further confirmed by ab-initio quantum mechanical calculations.

$^{2}J(^{31}P-^{207}Pb)$-coupling was observed in the spectra of lead(II) diethyl and di-iso-butylidithiophosphate complexes and additionally used in the assignment of terminal and bridging ligands in these compounds. The bridging ligand in the di-iso-butylidithiophosphate complex showed a complicated pattern of splittings of the resonance line due to J-couplings in different isotopomers in the binuclear complex.

$^{31}$P CP/MAS is a suitable method for studying the coordination of dialkyldithiophosphate ligands on a mineral surface. Its high sensitivity makes it possible to distinguish between different coordination modes on a mineral surface.
Surface adsorbed dithiophosphate complexes showed substantial inhomogeneous line broadening due to a distribution of surface sites with slightly different chemical environments. The more shielded phosphorus sites of the surface complexes, as compared to the potassium dialkyldithiophosphate salts were evidence of covalent bonding of the ligands to the mineral surface.

By comparing the isotropic chemical shifts of the polycrystalline dithiophosphate complexes with the corresponding surface adsorbed dithiophosphates, it was possible to assign a bridging coordination mode of the ligand to the surface of ZnS, while the coordination to the surface of PbS was suggested to be terminally chelating.

A bridging coordination seems more likely to occur on the surface of ZnS as the coordination number of the zinc atoms at the surface is three rather than two. For the larger lead atoms, which can adopt octahedral coordination, a reduction of the surface coordination number by two is possible, leading to the possibility of terminal coordination of the ligand on the surface.

The $^{31}$P NMR spectra revealed the presence of monothiophosphates and orthophosphates on the mineral surfaces. Disulfides were also present on the surface of ZnS, but could not be found on the surface of PbS. Bulk precipitates were detected on the surface of PbS, but not on the ZnS.

After three months of storing of PbS samples with surface adsorbed dialkyldithiophosphates, the chemisorbed ligands further hydrolyzed into monothiophosphates and orthophosphates. Diethyldithiophosphate, which is the least hydrophobic of the ligands, completely hydrolyzed during this time interval, while the most hydrophobic di-cyclo-hexyldithiophosphate did not hydrolyze at all, instead it formed a bulk precipitate of lead(II) di-cyclo-hexyldithiophosphate.
FUTURE RESEARCH

It was tested and proven that $^{31}$P solid-state NMR can be used to study adsorption processes at mineral surfaces. Therefore, it will be interesting to apply this method to real flotation systems. Dithiophosphates have so far not been studied as intensely as the analogous collector xanthate, so much research remains to be done on these systems.

Repetition of the experiments on ZnS at slower spinning speeds, to detect a larger number of spinning sidebands, can hopefully make $^{31}$P CSA analysis possible, and the distinct differences between terminal and bridging ligands in this case will make it possible to assign the correct coordination mode on the surface in the uncertain cases. Single-pulse $^{31}$P NMR experiments will reveal any liquid species on the surfaces, which are not detected by CP/MAS NMR.

Ex-situ investigations of dry samples can give results not relevant for the true flotation process, since a number of surface reactions can occur in the course of drying. Preliminary results show that with NMR it is possible to study systems “semi-in situ”, i. e. filtered, but not dried, which can give more reliable results, and changes in the surface complexation with time can be followed.

From previous studies on xanthates it is shown that pH, oxygen content and particle size are important factors for the flotation efficiency. Therefore, studies in which these parameters are varied can give new information on the behaviour of dithiophosphates.

In many flotation processes a mixture of xanthates and dithiophosphates are used because this mixture gives synergistic effects. NMR can be used to investigate the differences in surface adsorption between monocollector adsorption and multicollector adsorption. Even though $^{13}$C-labelled xanthates probably have to be synthesized to give detectable signals in the $^{13}$C spectra of mineral surface adsorbed species, their possible effect on the dithiophosphates can be studied indirectly in the form of changes in the $^{31}$P isotropic chemical shifts and CSA of the dithiophosphates.
The role of copper activation in the flotation of sphalerite can be studied, both with dithiohosphates and $^{13}$C-enriched xanthates.

Studies on $^{13}$C-labelled xanthates can give more detailed information on the coordination modes, and the role of oxygen, in connection with xanthate flotation, as well as confirm/reject previous flotation hypotheses based on results obtained by other methods. There has long been a debate about whether the disulfide has to be formed on the mineral surface to facilitate the froth flotation and with NMR this question can probably be answered.

In this study only synthetic and pure minerals have been studied, but natural minerals can also be studied. The surface area of those minerals is, however, smaller so the experimental time has to be increased in order to achieve a reasonable signal-to-noise ratio in the NMR spectra. The smaller surface area can on the other hand lead to less disordered surfaces and, hence, more narrow resonance lines, which give a relative increase in resolution, and the possibility of slower MAS NMR without interference of spinning sidebands and resonance lines. With slower MAS more spinning sidebands will be available for the CSA analysis.

In nature the minerals are rarely pure, but contains mixtures of different minerals, e. g. PbS/ZnS are often found together. Mixed mineral systems can also be studied with NMR, to see if and how the adsorption behavior changes, from the single-mineral case.

The study can be extended to other collectors and other minerals as well.

The theoretical aspects of the NMR technique can be further developed. In order to fully grasp the surface complexation it will be necessary to develop methods to calculate the dependence of the chemical shifts and chemical shift anisotropies to different structural factors, e. g. bond angles and bond lengths, of surface adsorbed complexes.
More advanced NMR experiments, like REDOR (Rotational Echo Double Resonance) [45], can be used to gain information on the adsorption in the galena system by the simultaneous excitation of $^{31}\text{P}$ and $^{207}\text{Pb}$ spins. Measurements of the heteronuclear $^{31}\text{P}-^{207}\text{Pb}$ dipole-dipole couplings can give information about interspin $^{31}\text{P}-^{207}\text{Pb}$ distances.
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