

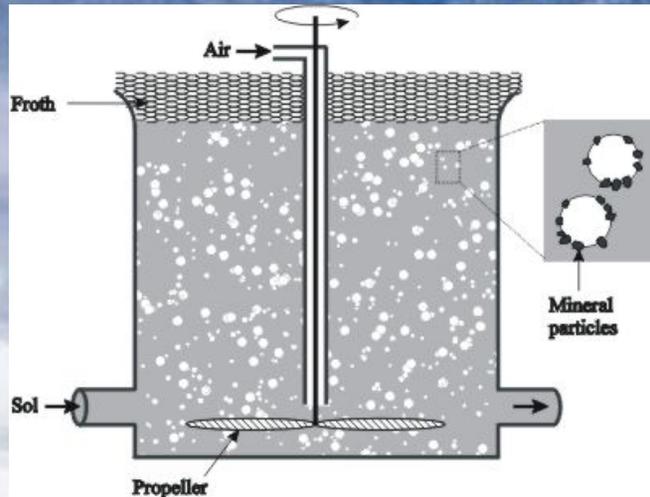
# Coordination chemistry of adsorption in froth flotation

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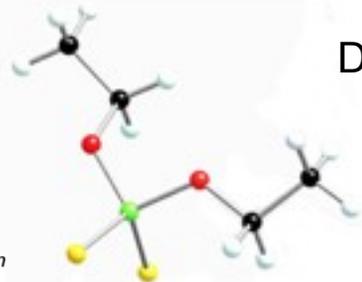
# Froth flotation

Used for separating valuable minerals from the gangue in an ore



Collectors added to the flotation tank adsorb to the surfaces of the valuable mineral particles, make them hydrophobic, and they attach to air bubbles and are collected in a froth.

<http://www.mpip-mainz.mpg.de/documents/akbu/media/flotation.jpg>



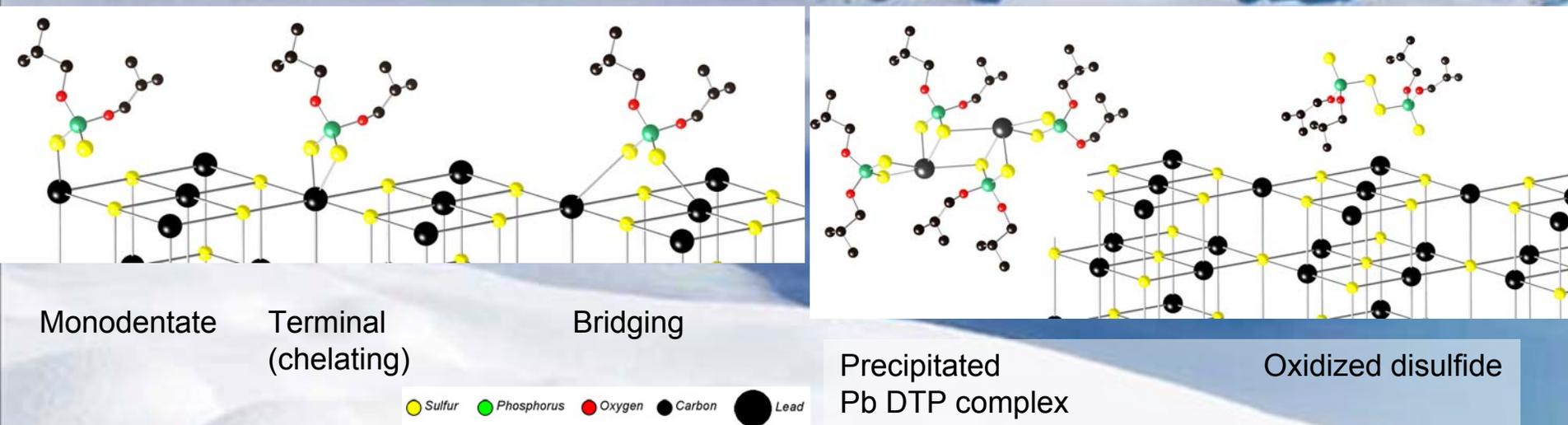
Diethyl dithiophosphate (DTP) collector used for sulfide mineral flotation

● Sulfur ● Phosphorus ● Oxygen  
● Carbon ○ Hydrogen

# Adsorption of collectors

One important step in the flotation process is the adsorption of a collector to the mineral surface

Possible coordination modes of DTP attached to a mineral surface (PbS)



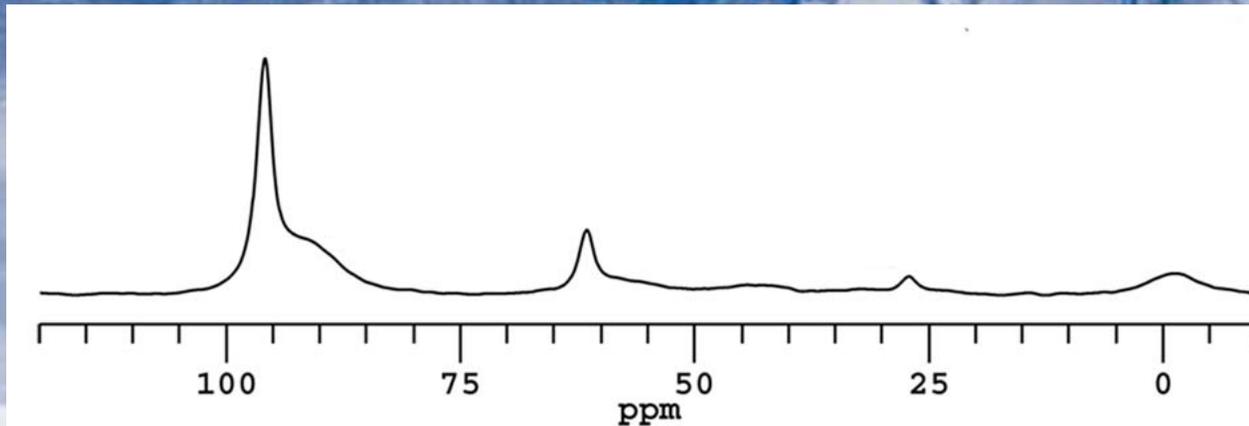
The electronic environment around the phosphorus is slightly different in the five situations above, which makes it possible to use  $^{31}\text{P}$  NMR to distinguish between them

# Nuclear Magnetic Resonance (NMR)

- \* When a sample is put into a magnetic field ( $B_0$ ) the nuclear spin moments become quantized and distribute among allowed energy levels (for  $^{31}\text{P}$  two, along and opposite  $B_0$ )
- \* The energy difference ( $\Delta E$ ) between the energy levels can be measured by applying an electromagnetic pulse with a frequency ( $\omega_0$ ) matching the resonance condition  $\Delta E = h\omega_0/2\pi$
- \*  $\omega_0$  is different for different nuclei  $\rightarrow$  element specific method ( $^{31}\text{P}$  145.7 MHz,  $^{13}\text{C}$  90.5 MHz, when  $B_0 = 8.46$  T)
- \*  $\omega_0$  is also affected by the chemical environment around nucleus, the so-called chemical shift,  $\delta$  (ppm)
- \* High sensitivity to small changes in electronic around the nucleus under study



# $^{31}\text{P}$ NMR spectrum of di-*iso*-propyl dithiophosphate adsorbed on PbS

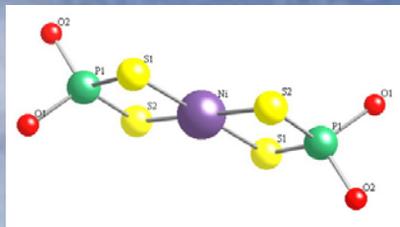


Physisorption or chemisorption?

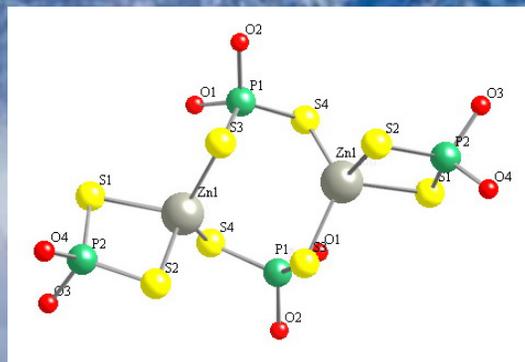
Metal-collector complexes or oxidized species?

What type of coordination?

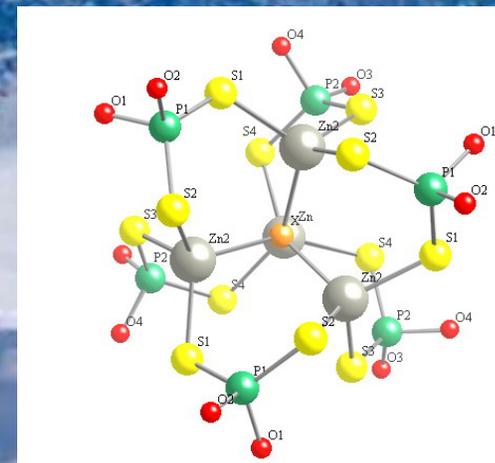
# Model systems



Ni DTP  
Terminal ligands



Zn DTP  
Terminal and bridging ligands



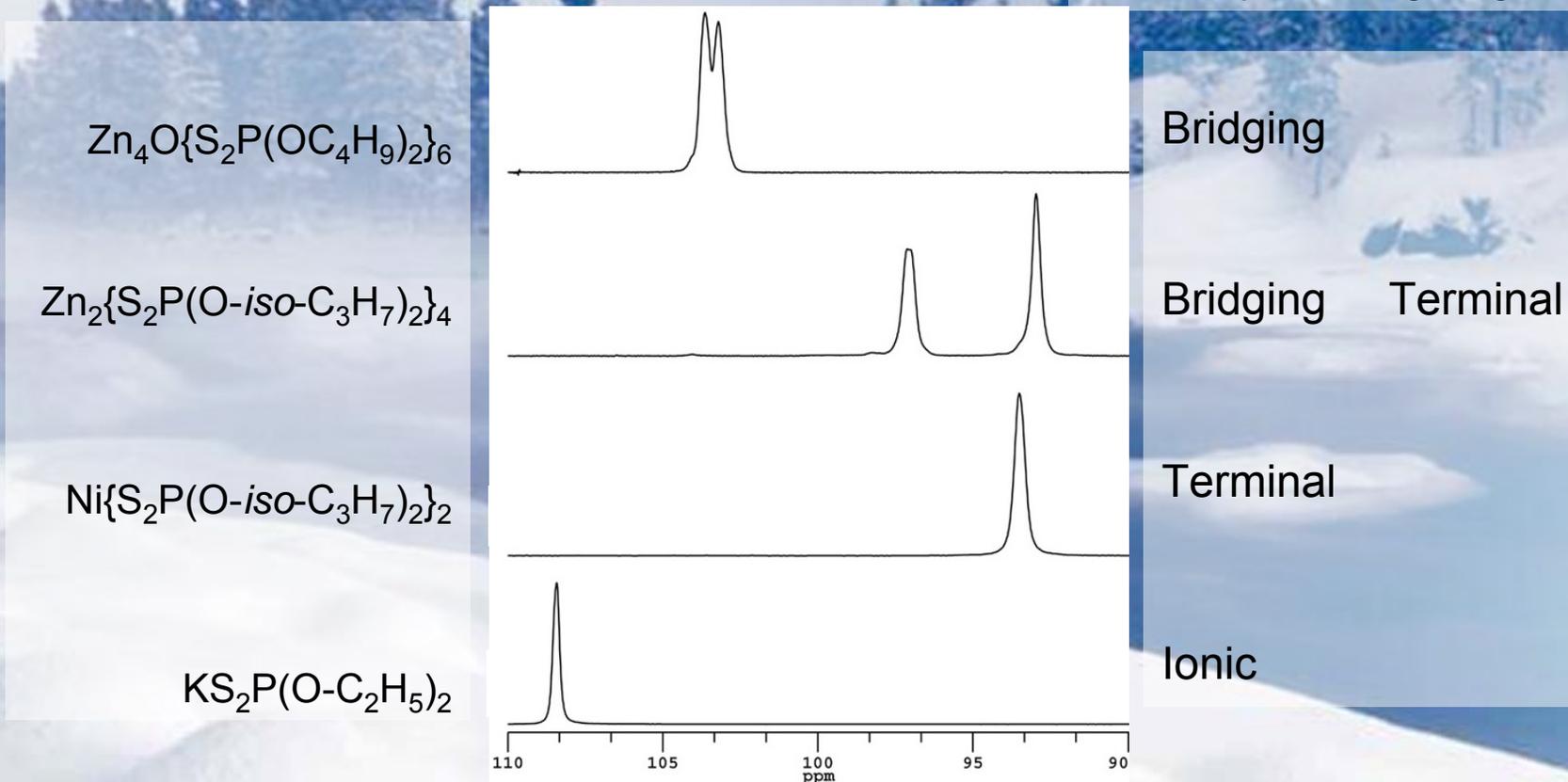
Zn<sub>4</sub>O DTP  
Bridging ligands

Small differences in electronic environment around the P atom in different coordinations give rise to different resonance signals in the NMR spectrum

Alkyl chains omitted for clarity

# $^{31}\text{P}$ NMR chemical shifts of different DTP model systems

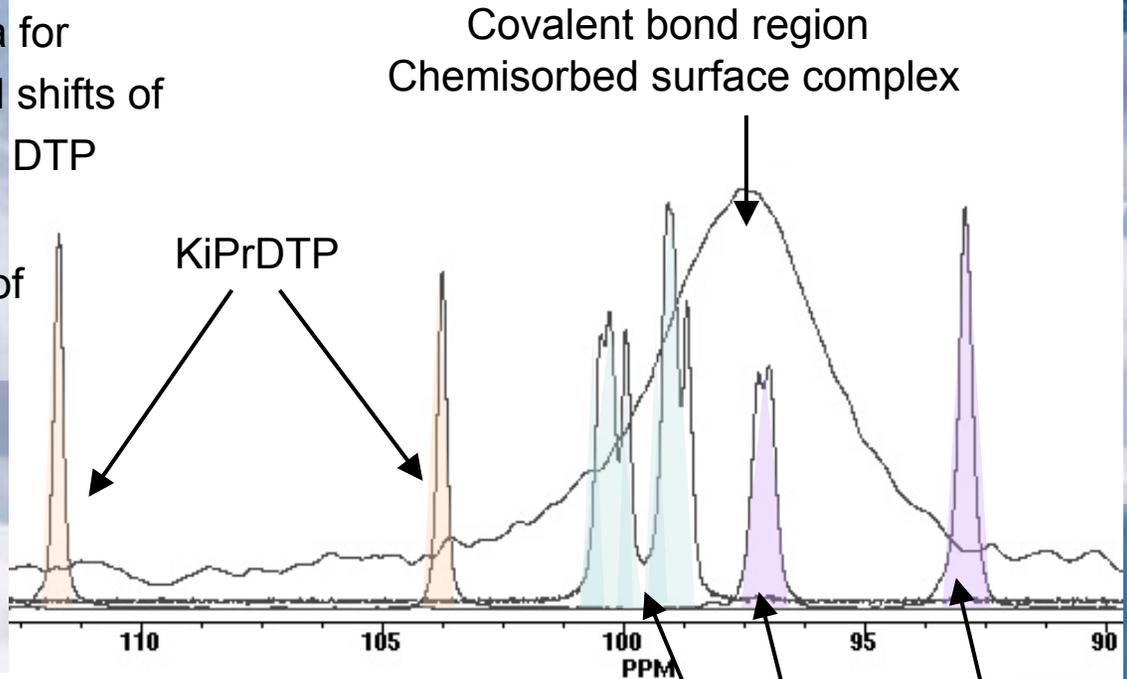
One example showing the general picture



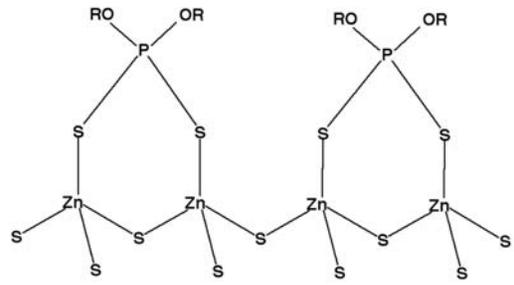
Terminal ligands have smaller chemical shifts than bridging ligands

# Di-*iso*-propyldithiophosphate adsorbed on ZnS

Overlapping spectra for comparing chemical shifts of surface coordinated DTP and model systems with known modes of coordination



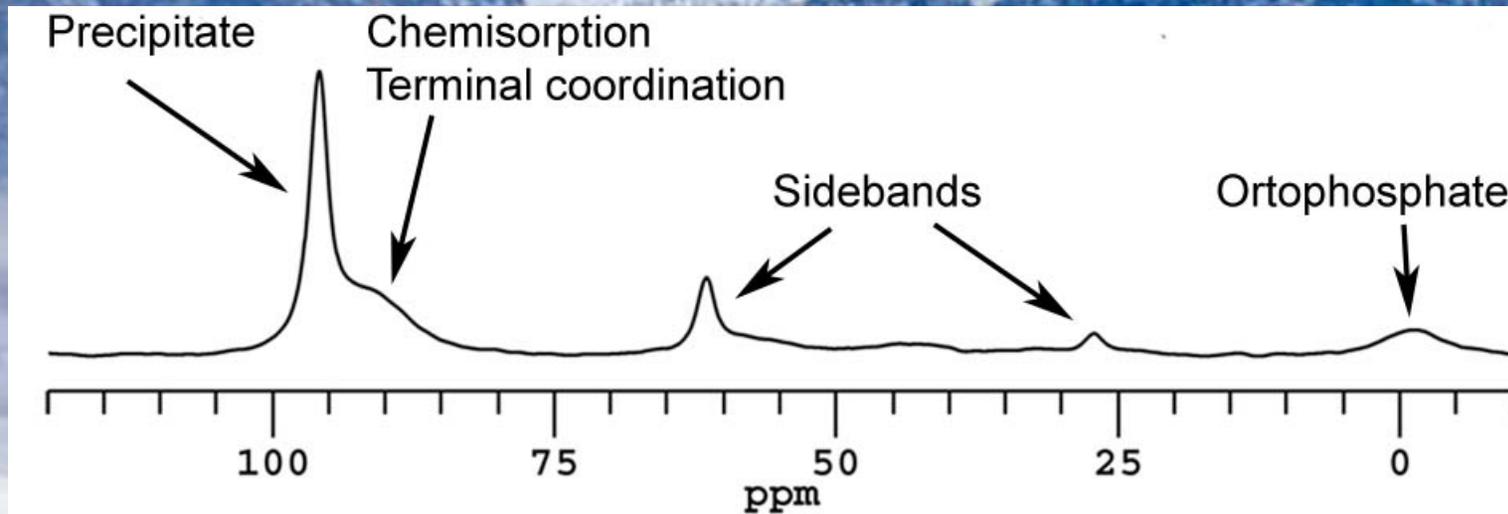
No precipitates of  $Zn_4O(DTP)_6$  or  $Zn_2(DTP)_4$  on the surface



**Bridging coordination of DTP to the ZnS surface**

Bridging ligands  $Zn_4O(DTP)_6$   $Zn_2(DTP)_4$   
Terminal ligands  $Zn_2(DTP)_4$

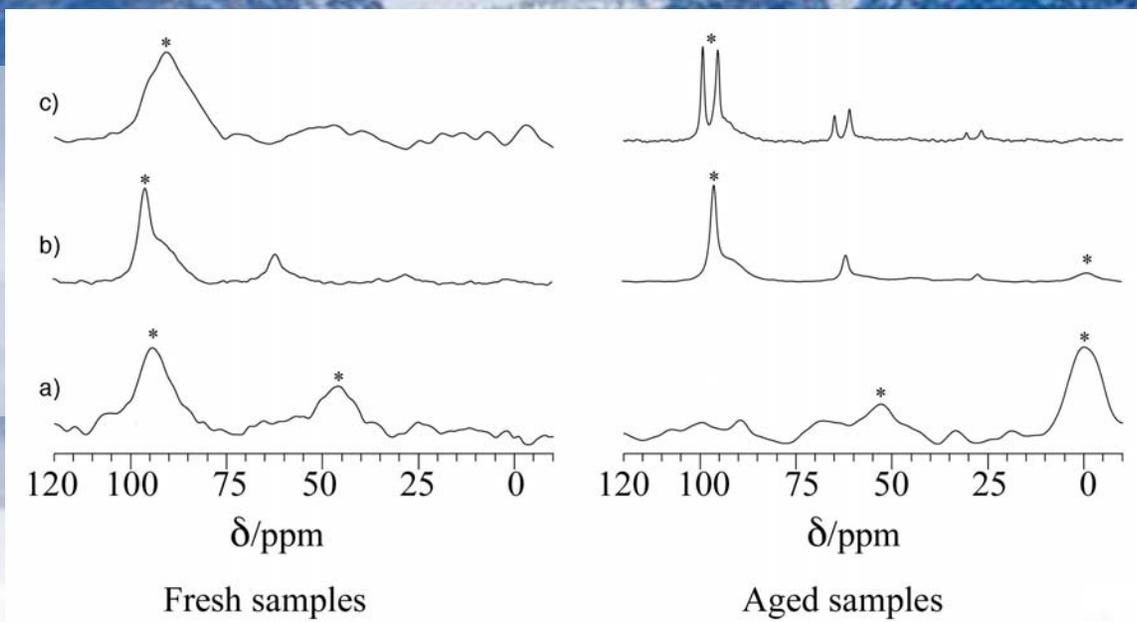
# Di-*iso*-propyldithiophosphate adsorbed on PbS



Oxidised DTP (disulfide) is not present ( $\approx 75\text{-}80$  ppm)

# Dithiophosphate adsorbed on PbS

Di-cyclo-hexyl  
Di-iso-propyl  
Di-ethyl



\* <sup>31</sup>P resonances

Surface complex  
 $\delta \approx 95$  ppm

Monothiophosphate  
 $\delta \approx 50$  ppm

Orthophosphate  
 $\delta \approx 0$  ppm

(3 months after the adsorption)

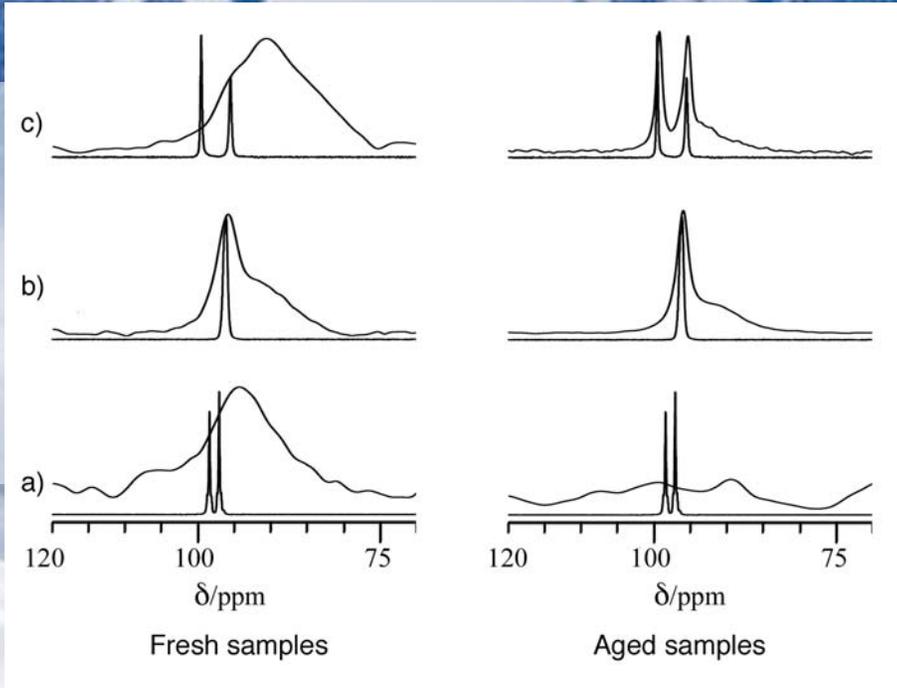


Monothiophosphate    Orthophosphate

More hydrolysis products form with time, the amount of which depends on the alkyl group

# Dithiophosphate adsorbed on PbS

Di-cyclo-hexyl  
 Di-iso-propyl  
 Di-ethyl

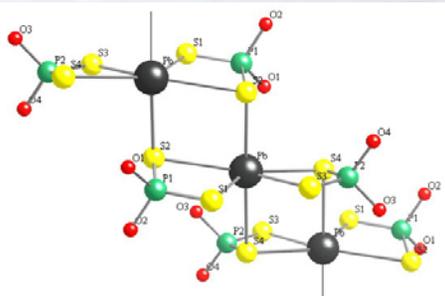


Precipitation forms with time

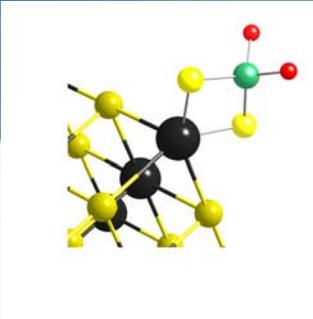
The amount of precipitation increases with time

No precipitation, complete hydrolysis

Sharp peaks: Polycrystalline Pb DTP complexes  
 Broad features: Chemisorbed surface complexes

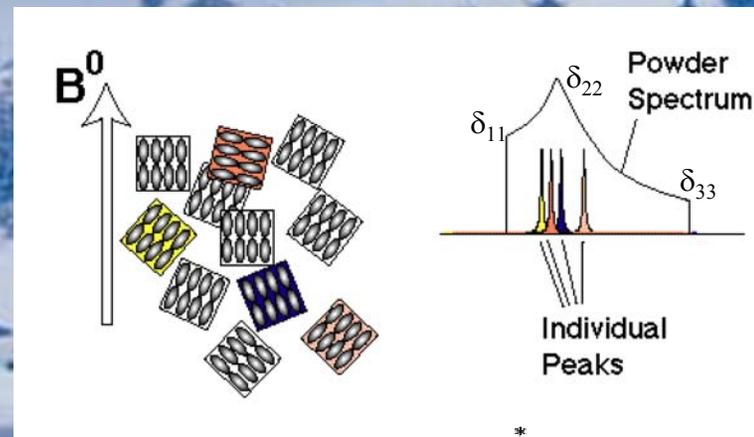


Terminal coordination of DTP to the PbS surface

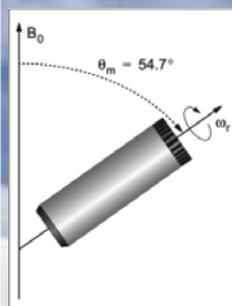


# Chemical shift anisotropy (CSA)

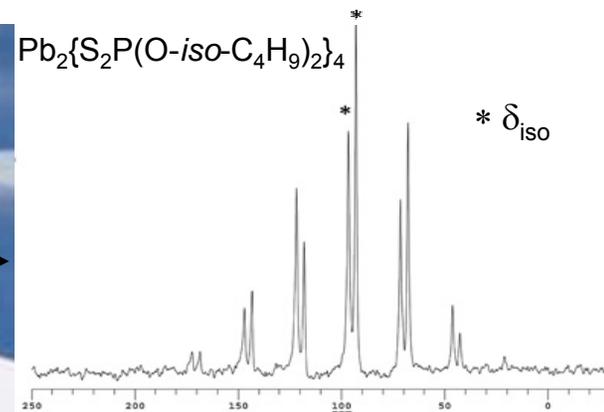
The resonance frequencies depend not only on the electronic environment around the nucleus, but also on the orientation of the individual crystallites relative to  $B_0$



Magic angle spinning (MAS) eliminates the anisotropy  $\rightarrow$  narrow resonance line at the isotropic chemical shift ( $\delta_{iso}$ ), flanked by spinning sidebands



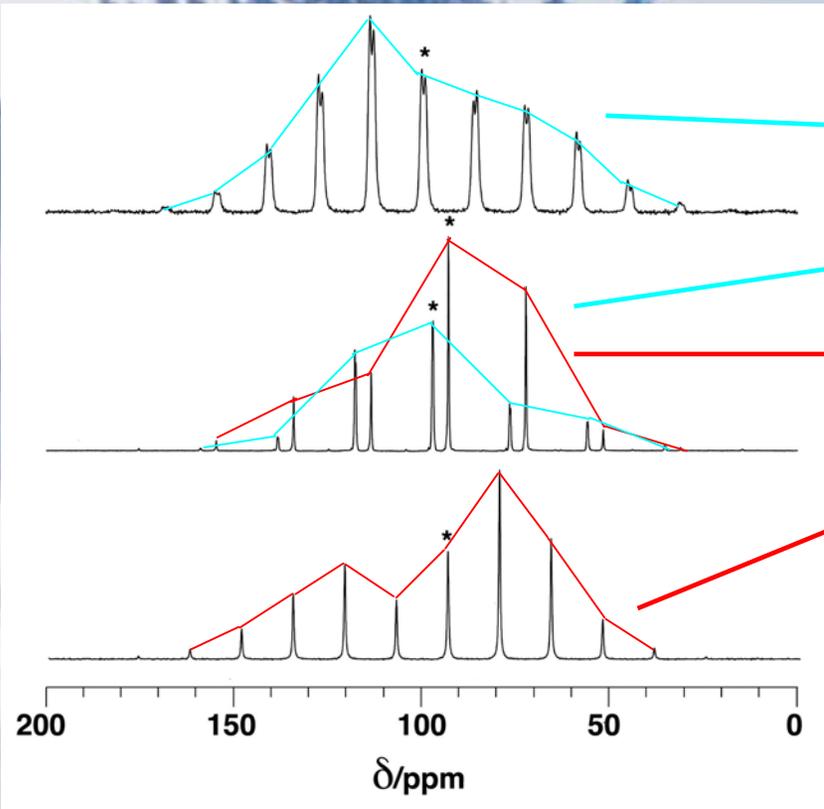
$\omega_r$  typically  
4-6 kHz



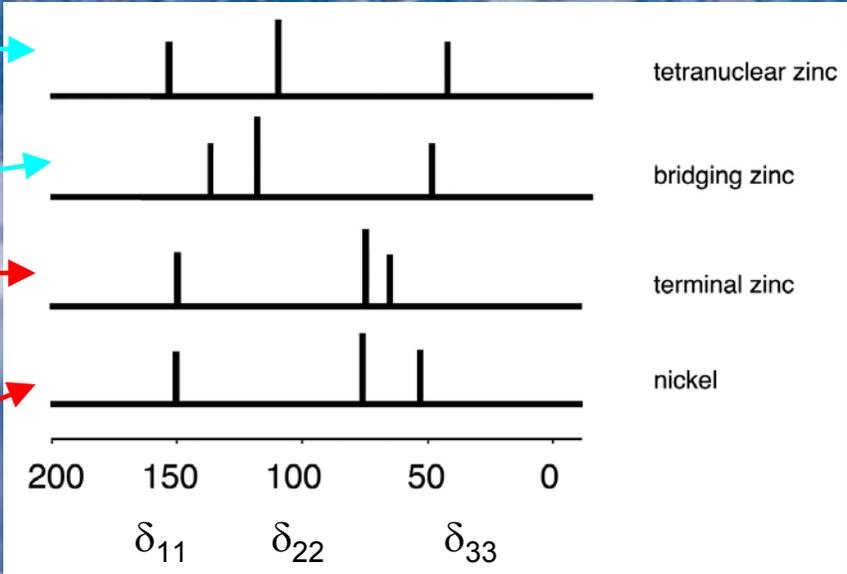
From the intensities of the spinning sidebands it is possible to get the values of  $\delta_{11}$ ,  $\delta_{22}$  and  $\delta_{33}$  and from them additional structural information

$$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33}) / 3$$

# Chemical shift anisotropy (CSA)



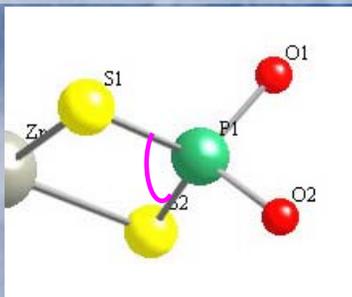
\* Isotropic chemical shifts



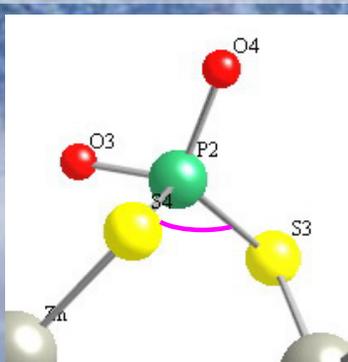
General shapes are similar for ligands with the same structural functions

# Dependence of $\delta_{nn}$ on S-P-S angle

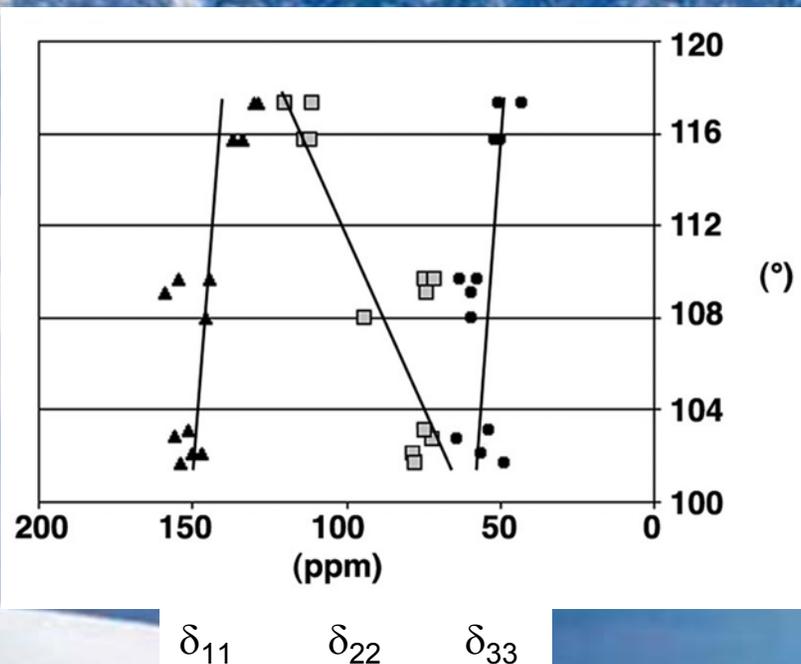
S-P-S angles in terminal ligands vary between  $102^\circ$ - $110^\circ$



S-P-S angles in bridging ligands vary between  $108^\circ$ - $121^\circ$



Zn and Ni dithiophosphates



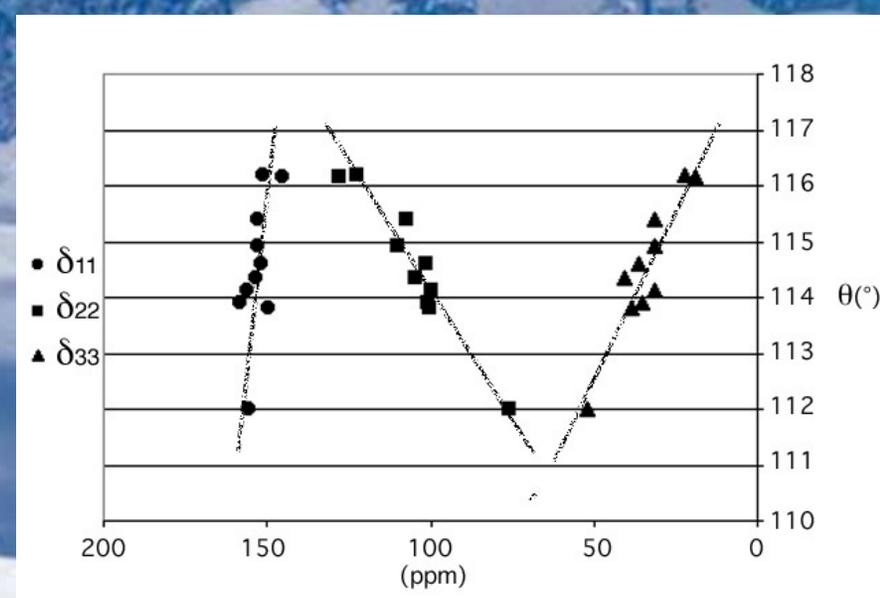
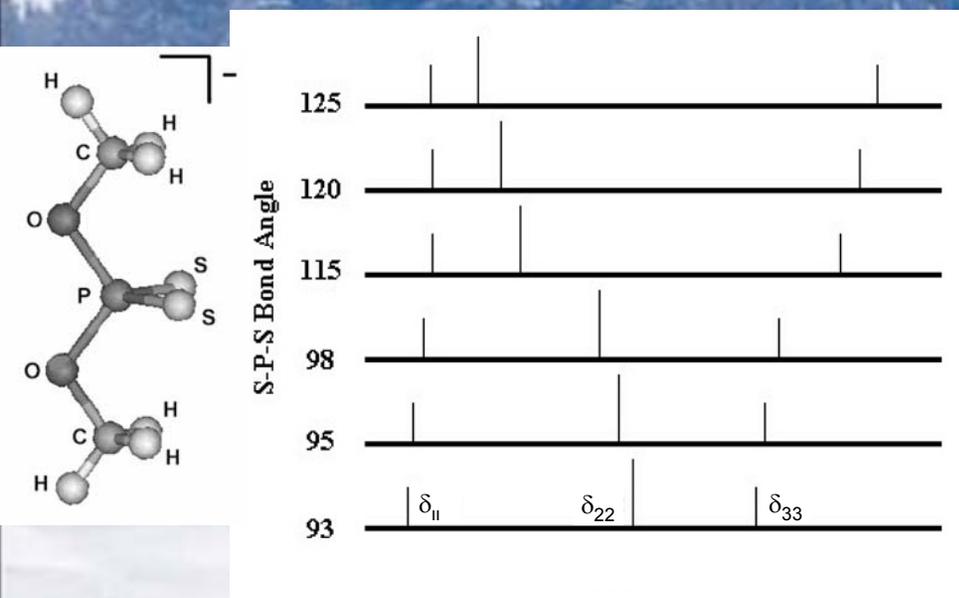
**Terminal ligands** have smaller S-P-S angles than bridging ligands and thus smaller  $\delta_{22}$  and **smaller**  $\delta_{iso}$ , as  $\delta_{11}$  and  $\delta_{33}$  do not change much

The larger the S-P-S angle the larger  $\delta_{22}$

# Dependence of $\delta_{nn}$ on S-P-S angle

*Ab-initio* on a model fragment

Pb DTPs



The larger the S-P-S angle the larger  $\delta_{22}$  and the smaller  $\delta_{33}$

As  $\delta_{22}$  and  $\delta_{33}$  change simultaneously but in opposite directions  $\delta_{iso}$  is almost conserved as S-P-S changes

# On-going research

To be presented at next Bergforsk meeting?

- \* CSA analysis to determine the S-P-S bite angle of DTP adsorbed to a mineral surface
- \* Quantitative studies of relative amounts of different surface species
- \* Studies of adsorption of DTP in mixed systems (mixed minerals / mixed collectors)

# Conclusions

- \* With  $^{31}\text{P}$  solid state NMR it is possible to study surface complexation
- \* It is possible to distinguish between different products on the surface: (ionic DTP, chemisorbed DTP, Metal DTP complexes, and different products of hydrolysis and oxidation), and also follow their transformation over time)
- \* It is possible to distinguish between different coordination modes of the chemisorbed ligands
- \* A linear correlation was found between the S-P-S angle and the chemical shift anisotropy parameter  $\delta_{22}$ , which can be used in the interpretation of the spectra of the surface complexes

# Conclusions

- \* The DTP ligands have a bridging coordination to the surface of ZnS
- \* The ligands have a terminal coordination to the surface of PbS, and precipitation of Metal DTP complexes occurs
- \* With time the DTP chemisorbed to PbS are transformed into Metal DTP, as well as hydrolyzed to mono- and orthophosphate species
- \* Traces of disulfide can be found on the surface of ZnS, but not on the surface of PbS

# Acknowledgements

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