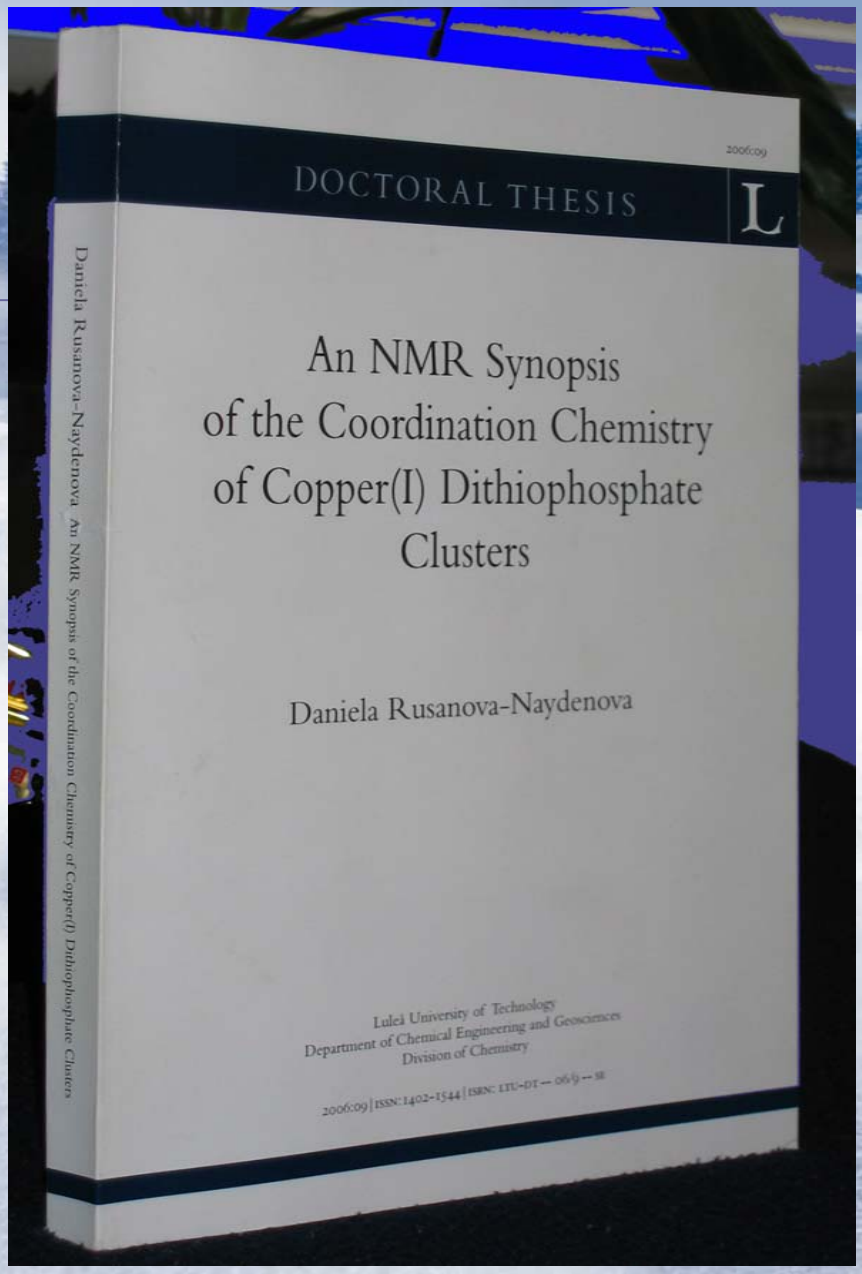

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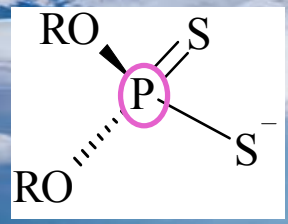
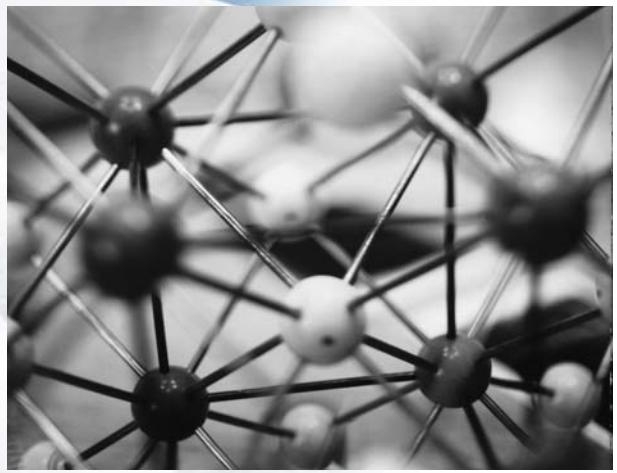
Why was it all done?

Dithiophosphate ion (R_2dtp) – L

R = alkyl



Cu (I)/ Cu(II)



$$4Cu^{II}(R_2dtp)_2 \rightleftharpoons 2\,[Cu^{II}(R_2dtp)_2 \ldots Cu^{II}(R_2dtp)_2] \rightleftharpoons 4Cu^{I}R_2dtp + 2(R_2dtp)_2$$

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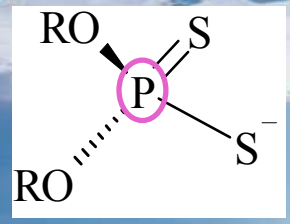
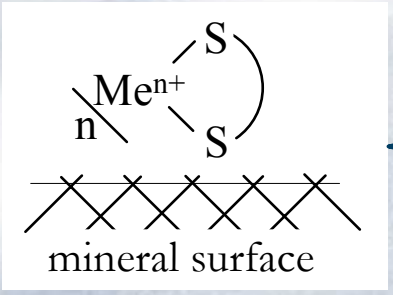
Literature data for Chalcocite/dtp:

Dithiophosphate ion (R_2dtp) – L

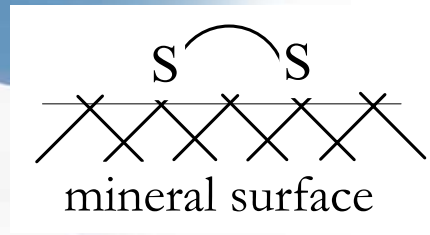
R = alkyl

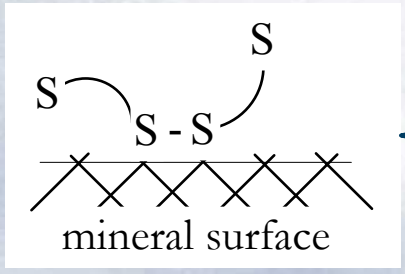


- Metal-collector species



Cu_2S/ Et_2dtp – reagents (chalcocite)





- An oxidised collector molecule

- A chemisorbed collector molecule

What is the structure of these species? How are they formed?

'Cu^I-DTP species' were found at Chalcocite Surfaces

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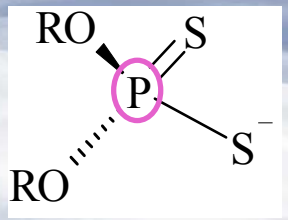
Syntheses of 'Cu^{I}-DTP species'

Dithiophosphate ion (R_2dtp) – L

R = Et, nPr, iPr, nBu, sBu, iBu, iAm, cHex



+

Cu (I)/ Cu(II)

Cu_4L_4, Cu_6L_6

$Cu_8L_6(S)$

Disulphides $(R_2dtp)_2$

~~CuL~~

~~CuL_2~~

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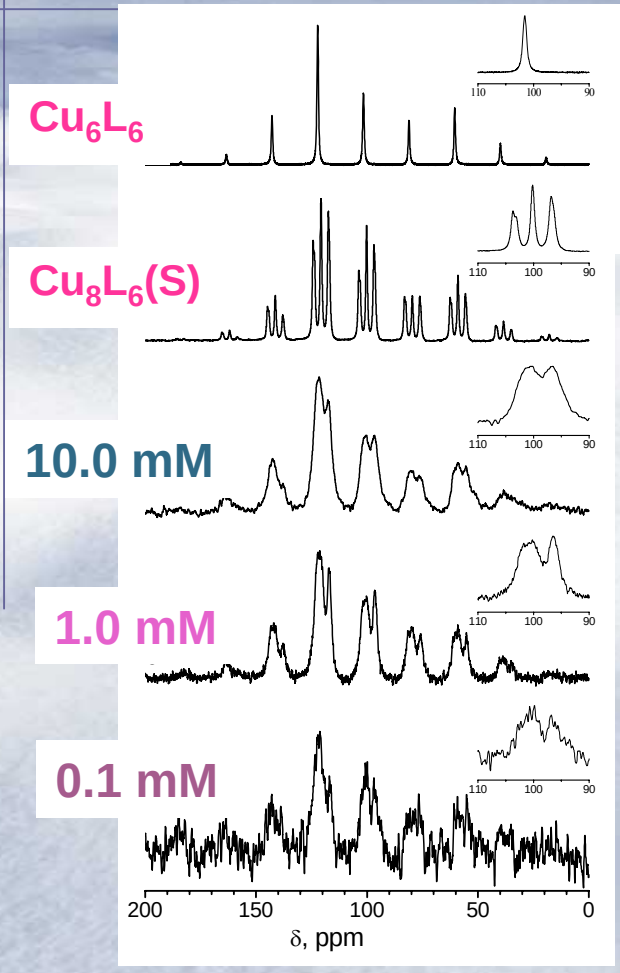
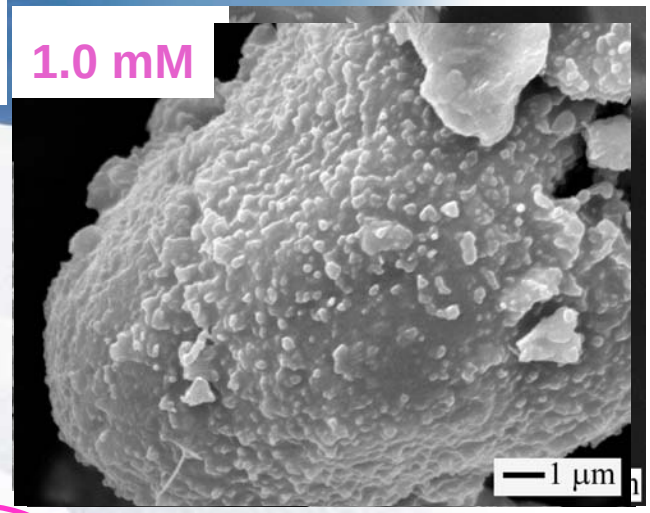
Results: Chalcocite/K*iBu*$_2$dtp



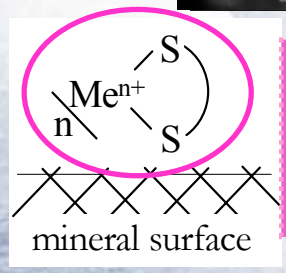
^{31}P MAS NMR spectra of K*iBu*$_2$dtp collector-treated chalcocite surfaces and the corresponding poly-nuclear systems

Chalcocite surfaces treated with **KiBu$_2$dtp**

1.0 mM



NMR data for the surface species and for the bulk Cu_6L_6 and $Cu_8L_6(S)$-species are very similar for the concentration range used.



'Cu^I-DTP species': Cu$_6$L$_6$ and Cu$_8$L$_6$(S) (0.3 :0.7) (L = iBu$_2$dtp)

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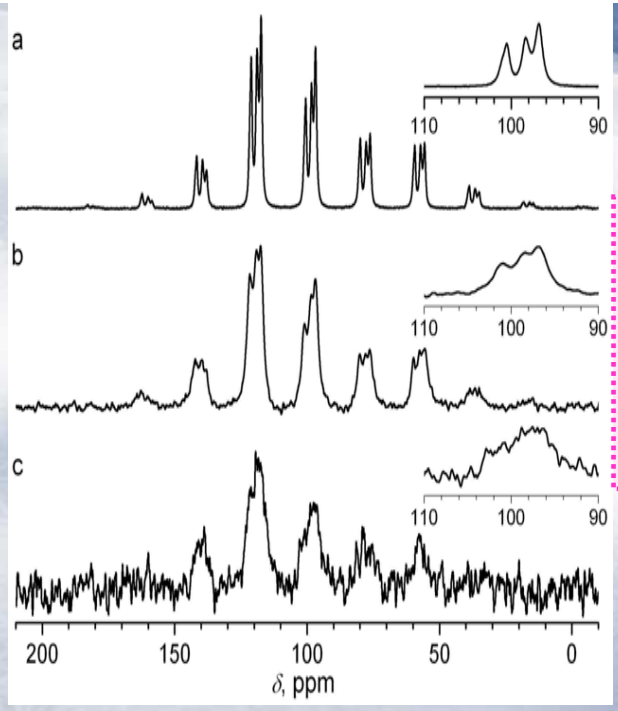
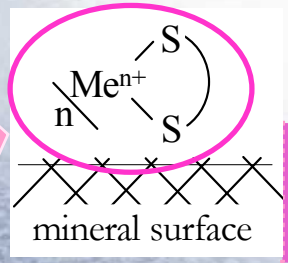
Results: Chalcocite / *iAm*$_2$dtp-disulphide

^{31}P MAS NMR spectra of $Cu_8L_6(S)$ (a), KL-treated- (b) and L_2-treated- (c) chalcocite surfaces

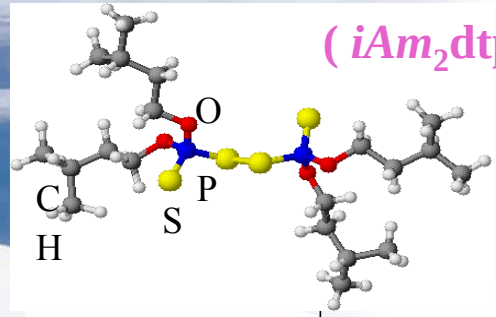


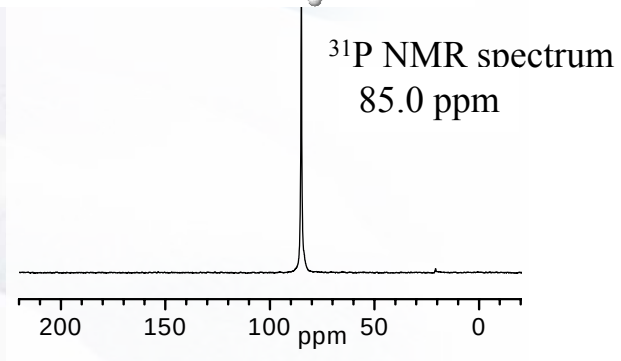
NMR data for the surface species and for the bulk $Cu_8L_6(S)$ -species are very similar.



'Cu^I-DTP species': $Cu_8L_6(S)$ (L = iAm$_2$dtp)

(*iAm*$_2$dtp)$_2$





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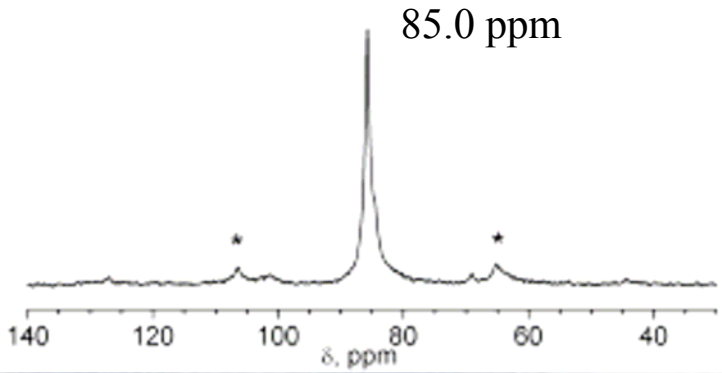
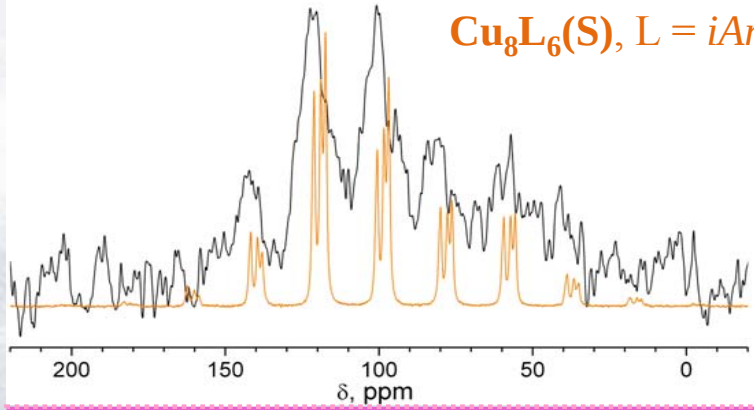
Results: Mineral surface nature

^{31}P NMR spectrum of **L_2**-treated **Cu_2O** shows only the presence of **L_2** (L = nBu_2dtp) (*-L_2-sidebands)



Presence of sulphur is a necessary condition for formation of the 'Cu^{I}-DTP species' at the mineral surface.

^{31}P NMR spectrum of **KL**-treated **ZnS(Cu)** (in black) shows the presence of **$Cu_8L_6(S)$** (L = iAm_2dtp)



Presence of copper at sphalerite surfaces ensures the formation of the 'Cu^{I}-DTP species' at the mineral surface.

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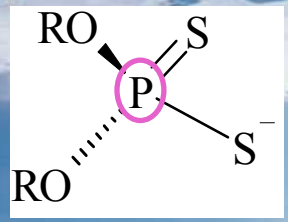
Results: Adsorption of dtp - reagents

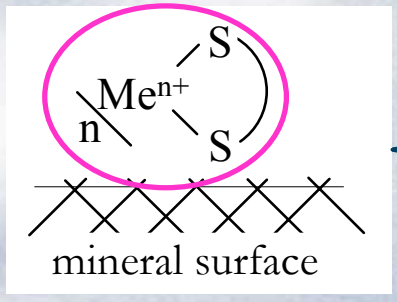
Dithiophosphate ion (R_2dtp) – L

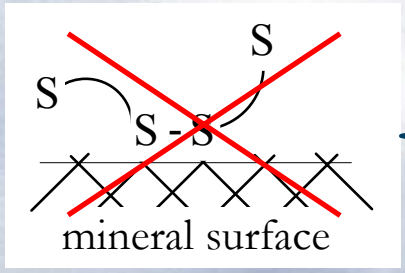
R = Et, nPr, iPr, nBu, sBu, iBu, iAm, cHex



- Metal-collector species

Cu_2S/ R_2dtp – reagents (chalcocite)





- A chemisorbed collector molecule

Poly-nuclear copper-collector systems

- An oxidised collector molecule

'Cu^I-DTP species' found at Chalcocite Surfaces

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Results: a model of interaction between *dtp* – reagents and chalcocite surfaces

$$Cu^{+}_{\underline{surface}} + L^{-} \leftrightarrow \{CuL\}^{*}_{\underline{surface}}$$

$$2Cu^{2+}_{\underline{surface}} + 4\,L^{-} \leftrightarrow 2\,\{CuL_2\}^{*}_{\underline{surface}}$$

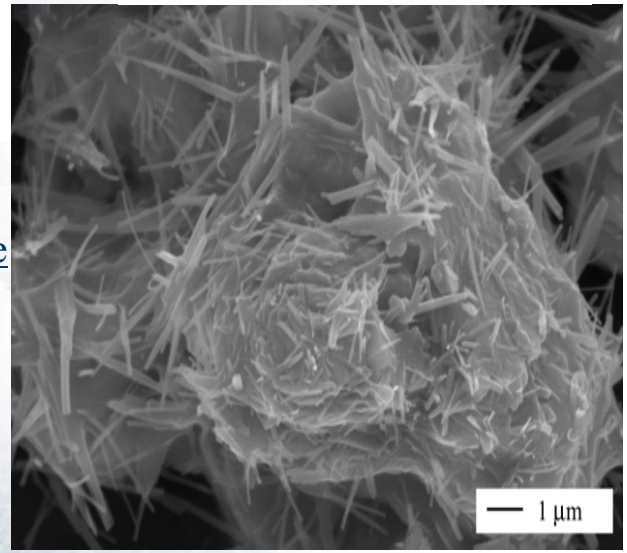
Surface Self-red-ox reaction ($L = R_2dtp^{-}$)

$$\{CuL_2 \ldots CuL_2\}^{*}_{\underline{surface}} \leftrightarrow 2\,\{CuL\}^{*}_{\underline{surface}} + L_2$$

$$\{L_2\}_{\underline{surface}} + 2Cu^{+}/Cu^{2+}_{\underline{surface}} \leftrightarrow 2\,\{CuL\}^{*}_{\underline{surface}}$$

{CuL} ≡ Cu_4L_4, Cu_6L_6 or $Cu_8L_6(S)$ or mixtures of these is formed depending on the type of *R* in the R_2dtp – collector.

A chalcocite surface treated with **$KiAm_2dtp$**



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What more do we know about the Chalcocite-R_2dtp system?

- Structures of '*Cu^I-dtp species*' at chalcocite surfaces are defined - Cu_4L_4, Cu_6L_6, $Cu_8L_6(S)$, L = R_2dtp. Mixtures of these are formed depending on the type of *R* in the R_2dtp – collector.
- The presense of sulphur at the mineral surfaces induses the formation of different copper-dtp species.
- Dtp-disulphides are reduced at chalcocite surfaces and the same complex '*Cu^I-dtp species*' are formed.
- Model of interaction of copper and dtp at a copper sulphide mineral surface is establish.

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Acknowledgements

SSF, LKAB, Boliden, Sweden

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LKAB

boliden

Thank You

Cheminova Agro, Denmark

CHEMINOVA

Calculations…
Theoretical *monolayer* (ML)– coverage

If a *dtp*-molecules occupies 35,4 Å^2 (S. Grano, 1988) and we have a 1g of Cu_2S (synthetic) with a surface area of 1 m^2/g (BET measurements) then:

n = 1.10^{20} Å^2/35,4 Å^2 = 0.02825 .10^{20} *dtp*-molecules

moles = 0.02825 .10^{20} molecules/ Na = 4,6927.10^{-6} *dtp*-moles

If a 50 ml aqueous solution is used:

c = 4,6927.10^{-6} *dtp*-moles / 0,050 = 9.3854. 10^{-5} M

Or

c is about 0.094 mM.

ICP data of the aqueous *dtp*-solutions after the adsorption show no presence of phosphorus species

A concentration equal to 0.10 mM was used when chalcocite surfaces were treated or conditions at which 0.1/ 0.094 = 1.0638 ML could be formed