

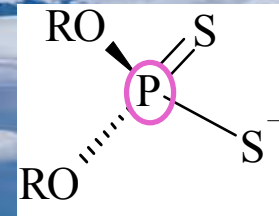
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Luleå University of Technology
Luleå, SWEDEN

Why was it all done?

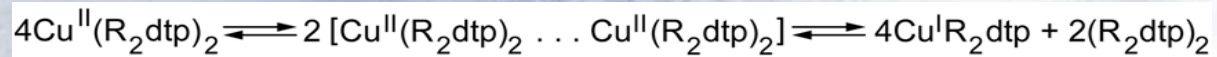
Dithiophosphate ion (R_2dtp) – L
R = alkyl



Natural Chalcocite



Cu (I)/ Cu(II)

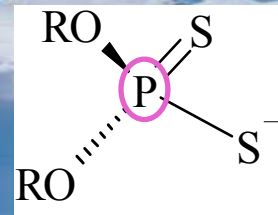


Literature data for Chalcocite/dtp:

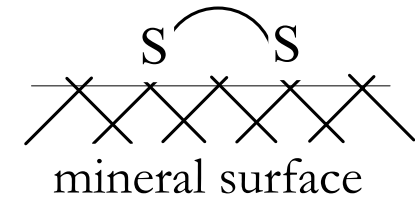
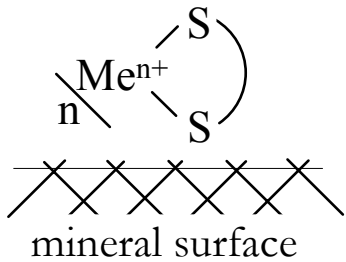
Dithiophosphate ion (R_2dtp) – L

$R = \text{alkyl}$

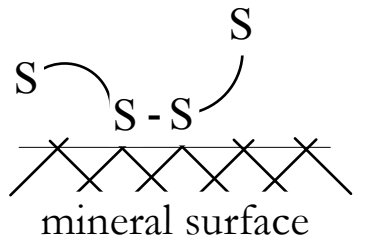
- Metal-collector species



Cu_2S / Et_2dtp – reagents
(chalcocite)



- A chemisorbed collector molecule

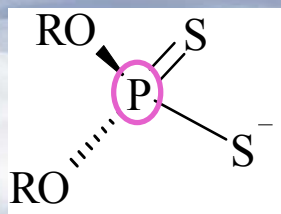


- An oxidised collector molecule

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

‘Cu^I-DTP species’
were found at Chalcocite Surfaces

Syntheses of 'Cu^I-DTP species'



+

Cu (I)/ Cu(II)



Dithiophosphate ion (R_2dtp) – L
 $R = Et, nPr, iPr, nBu, sBu, iBu, iAm, cHex$

Cu_4L_4, Cu_6L_6

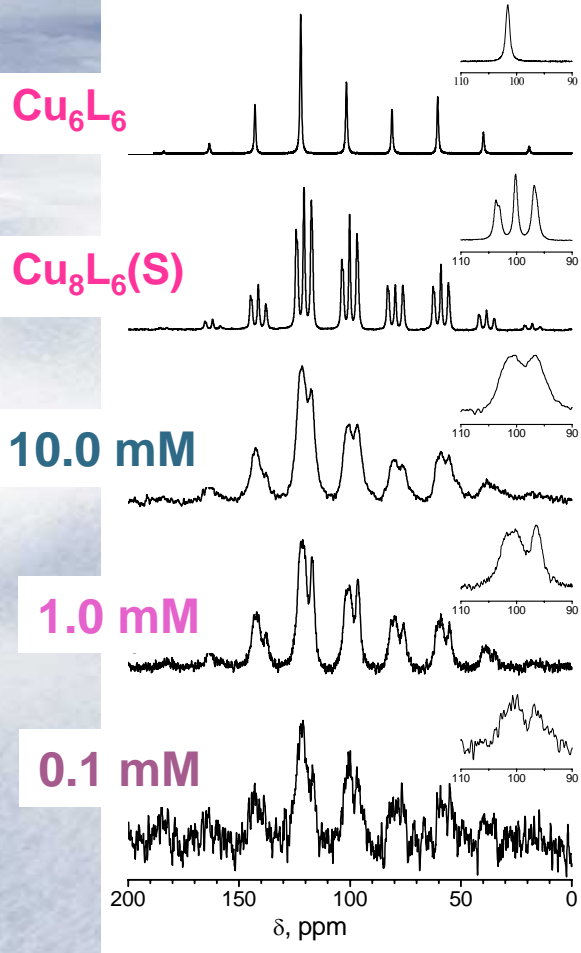
$Cu_8L_6(S)$

Disulphides
 $(R_2dtp)_2$

~~CuL~~

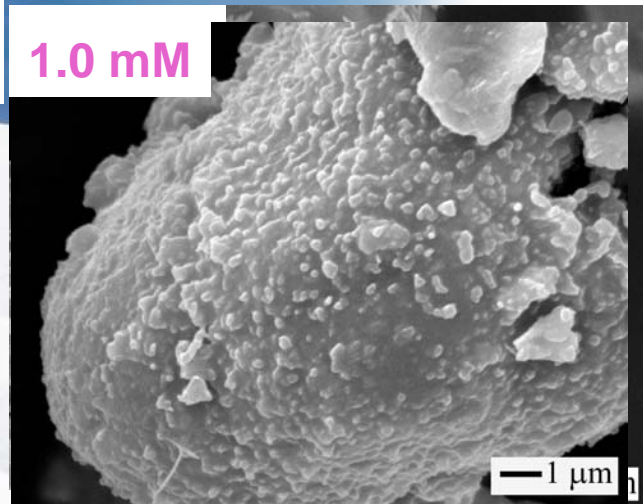
~~CuL₂~~

Results: Chalcocite/*KiBu*₂dtp

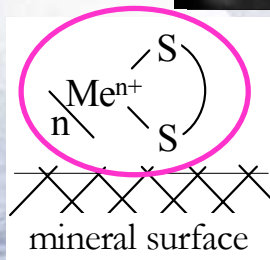


³¹P MAS NMR spectra of *KiBu*₂dtp collector-treated chalcocite surfaces and the corresponding poly-nuclear systems

Chalcocite surfaces treated with *KiBu*₂dtp



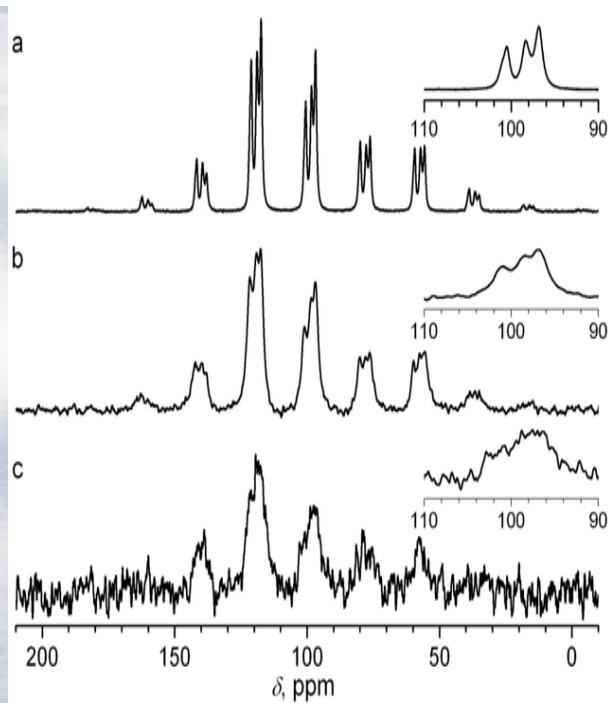
NMR data for the surface species and for the bulk Cu_6L_6 and $Cu_8L_6(S)$ -species are very similar for the concentration range used.



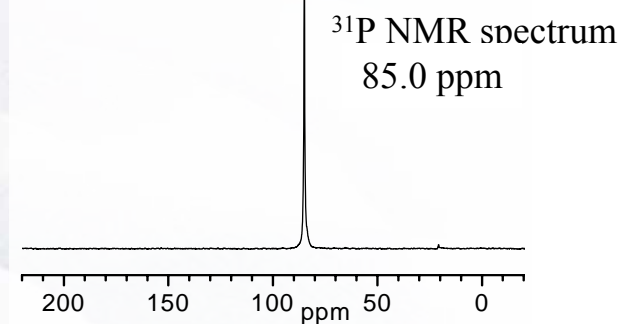
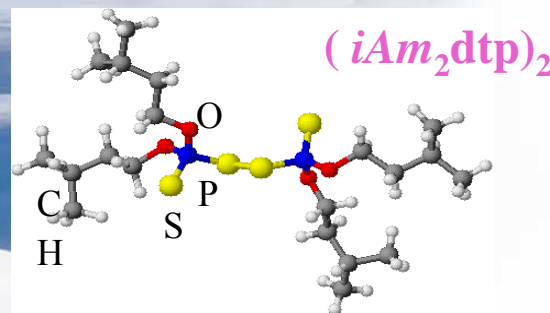
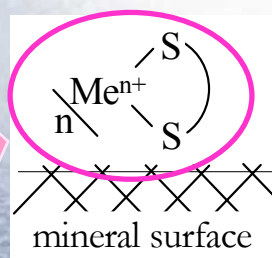
'Cu^I-DTP species': Cu_6L_6 and $Cu_8L_6(S)$ (0.3 : 0.7) (L = *iBu*₂dtp)

Results: Chalcocite/*iAm*₂dtp-disulphide

³¹P MAS NMR spectra of **Cu₈L₆(S)** (a), **KL**-treated- (b) and **L₂**-treated- (c) chalcocite surfaces



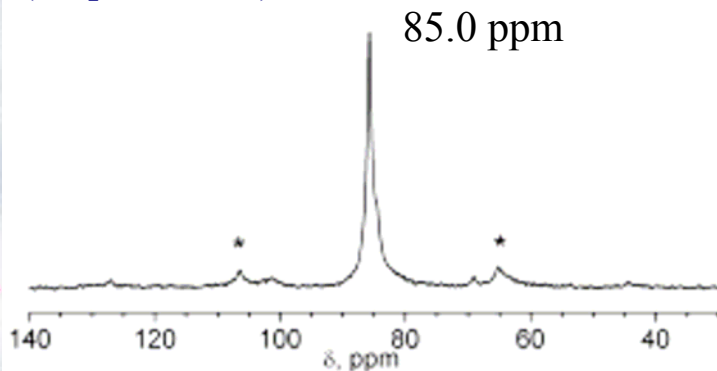
NMR data for the surface species and for the bulk Cu₈L₆(S) -species are very similar.



'Cu^I-DTP species':
Cu₈L₆(S) (L = *iAm*₂dtp)

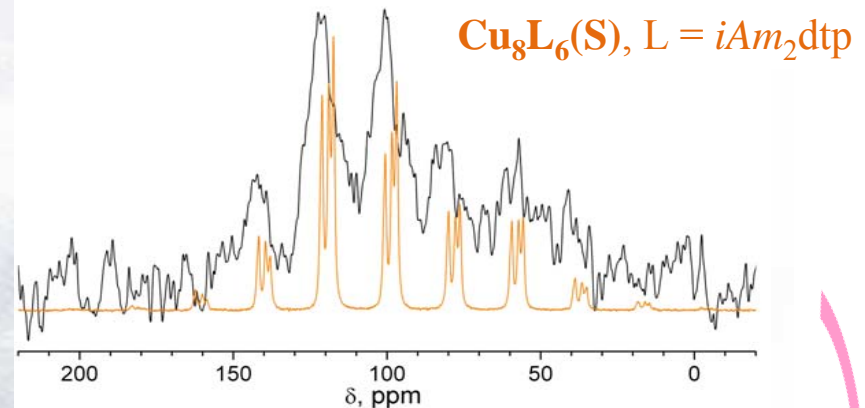
Results: Mineral surface nature

^{31}P NMR spectrum of L_2 -treated Cu_2O shows only the presence of L_2 ($\text{L} = n\text{Bu}_2\text{dtp}$) (*- 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 $\text{ZnS}(\text{Cu})$ (in black) shows the presence of $\text{Cu}_8\text{L}_6(\text{S})$ ($\text{L} = i\text{Am}_2\text{dtp}$)

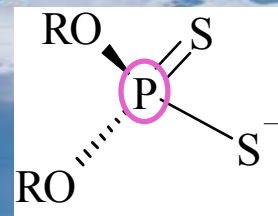


Presence of copper at sphalerite surfaces ensures the formation of the 'Cu^I-DTP species' at the mineral surface.

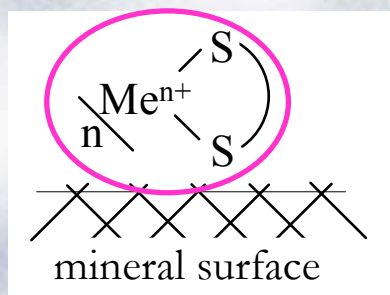
Results: Adsorption of dtp - reagents

Dithiophosphate ion (R_2dtp) – L

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

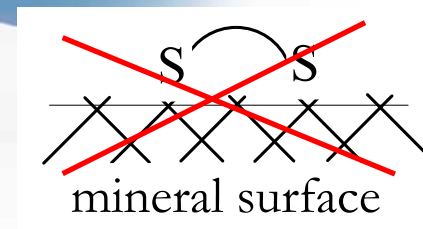


- Metal-collector species

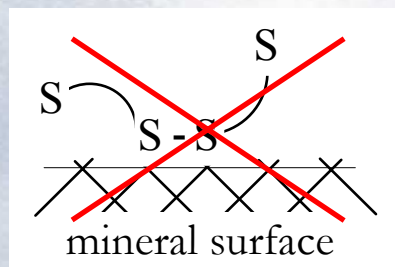


Poly-nuclear copper-collector systems

Cu_2S / R_2dtp – reagents (chalcocite)



- A chemisorbed collector molecule



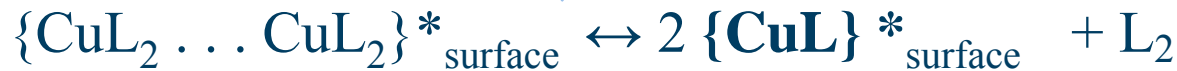
- An oxidised collector molecule

‘Cu^I-DTP species’ found at Chalcocite Surfaces

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

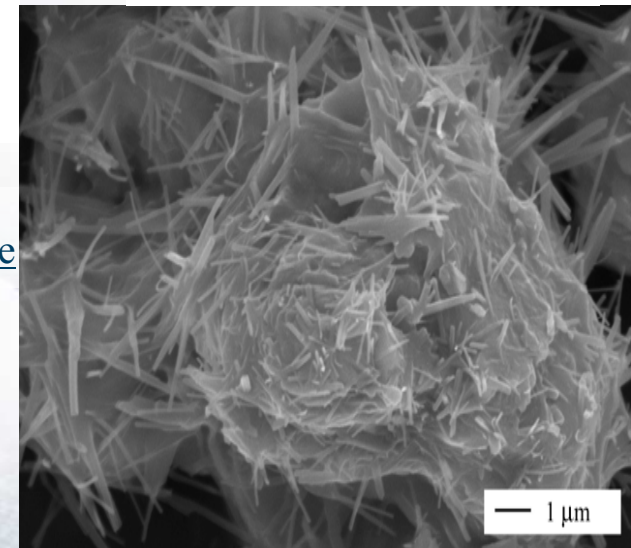


Surface Self-red-ox reaction ($\text{L} = \text{R}_2\text{ntp}^-$)



$\{\text{CuL}\} \equiv \text{Cu}_4\text{L}_4, \text{Cu}_6\text{L}_6$ or $\text{Cu}_8\text{L}_6(\text{S})$
or mixtures of these is formed depending
on the type of *R* in the R_2ntp – collector.

A chalcocite surface
treated with KiAm_2ntp



What more do we know about the **Chalcocite- R_2 ntp** system?

- Structures of ' Cu^I -ntp species' at chalcocite surfaces are defined - Cu_4L_4 , Cu_6L_6 , $Cu_8L_6(S)$, $L = R_2ntp$. Mixtures of these are formed depending on the type of R in the R_2ntp – collector.
- The presence of sulphur at the mineral surfaces induces the formation of different copper-ntp species.
- Ntp-disulphides are reduced at chalcocite surfaces and the same complex ' Cu^I -ntp species' are formed.
- Model of interaction of copper and ntp at a copper sulphide mineral surface is establish.



Acknowledgements

L

SSF, LKAB, Boliden, Sweden



Thank You

Cheminova Agro, Denmark



Calculations...

Theoretical monolayer (ML)- coverage

If a *ntp*-molecules occupies $35,4 \text{ \AA}^2$ (S. Grano, 1988) and we have a 1g of Cu_2S (synthetic) with a surface area of $1 \text{ m}^2/\text{g}$ (BET measurements) then:

$$n = 1 \cdot 10^{20} \text{ \AA}^2 / 35,4 \text{ \AA}^2 = 0,02825 \cdot 10^{20} \text{ ntp-molecules}$$

$$\text{moles} = 0,02825 \cdot 10^{20} \text{ molecules} / \text{Na} = 4,6927 \cdot 10^{-6} \text{ ntp-moles}$$

If a 50 ml aqueous solution is used:

$$c = 4,6927 \cdot 10^{-6} \text{ ntp-moles} / 0,050 = 9,3854 \cdot 10^{-5} \text{ M}$$

Or

c is about **0.094 mM**.

A concentration equal to 0.10 mM was used when chalcocite surfaces were treated or conditions at which $0,1 / 0,094 = \mathbf{1,0638 \text{ ML}}$ could be formed

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