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## Radical cation salts of TTF donors with XF<sub>6</sub> (X = Re, Ta) anions

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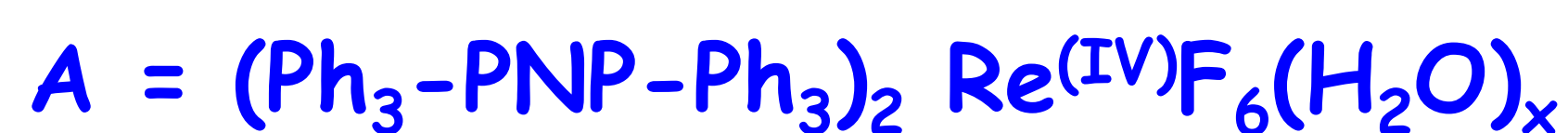
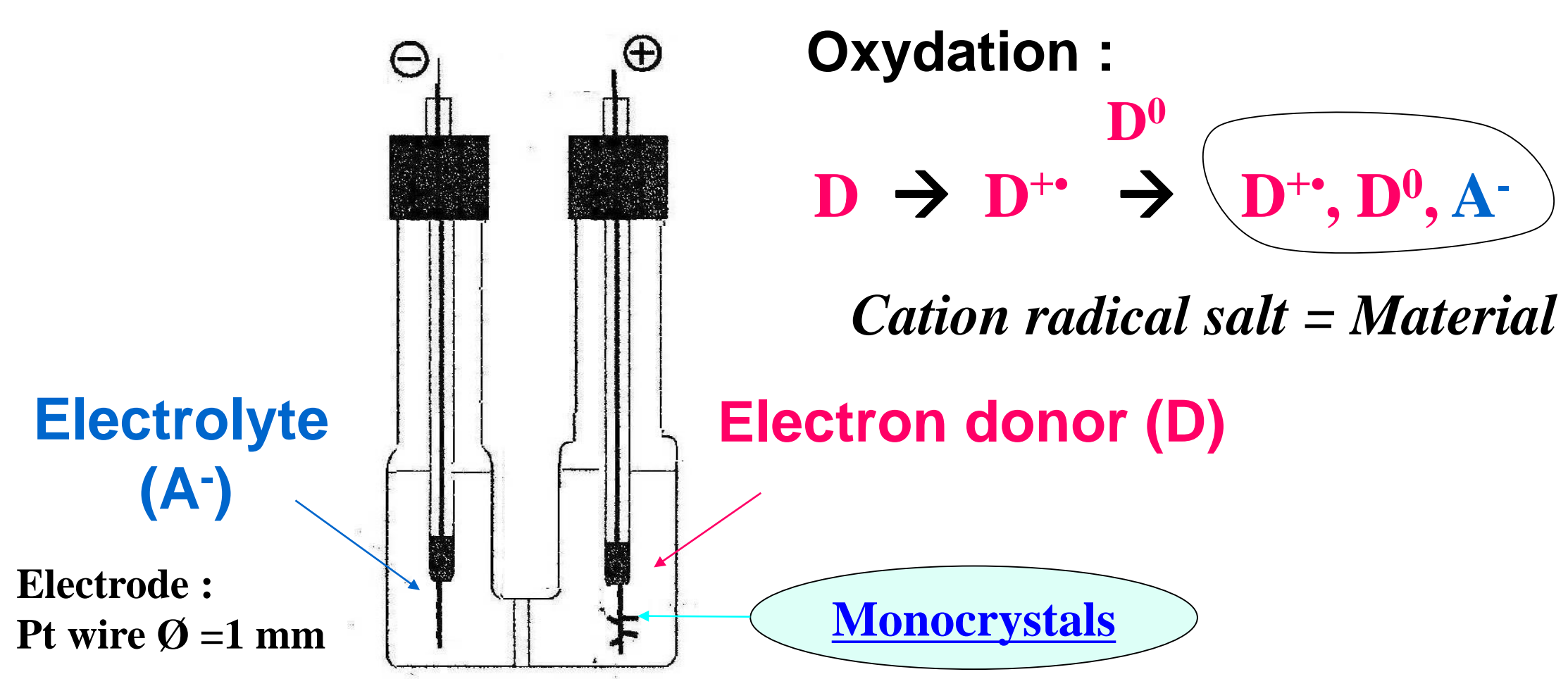
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### Electrocrystallization set up [1]



TETRAMETHYL-TETRATHIAFULVALENE

Solvent :  $\text{CH}_3\text{CN}/1.1.2 \text{ TCE } 11/1 \text{ mL}$

$T = 3^\circ \text{ C}$ ,  $I = 1$  to  $5 \mu\text{A}$



Unit cell, RT,  $\lambda = 1.540598$  :

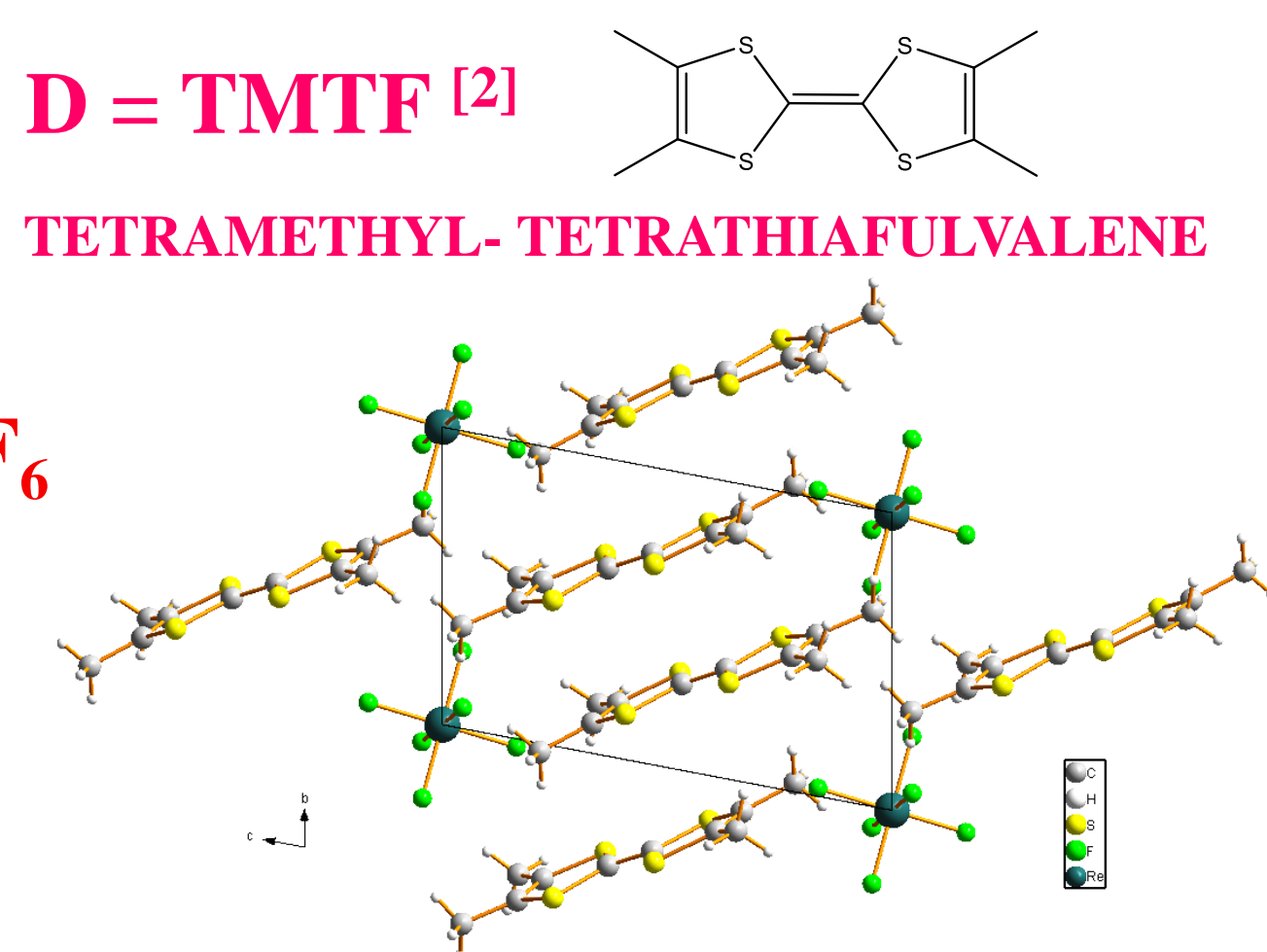
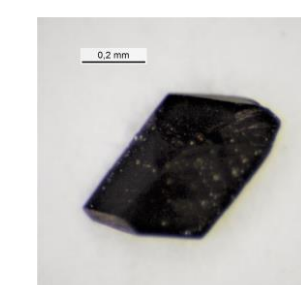
$a = 7.9941(17) \text{ \AA}$   $\alpha = 79.85(2)^\circ$

$b = 8.121(2) \text{ \AA}$   $\beta = 89.145(18)^\circ$

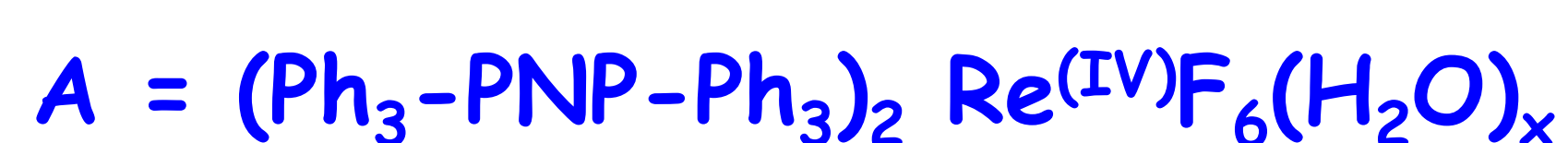
$c = 11.372(3) \text{ \AA}$   $\gamma = 65.466(18)^\circ$

$V = 659.71(30) \text{ \AA}^3$

Triclinic system, P-1



Strong dimerization  $\rightarrow$  insulating 1D system



TETRAMETHYL-TETRASELENAFULVALENE

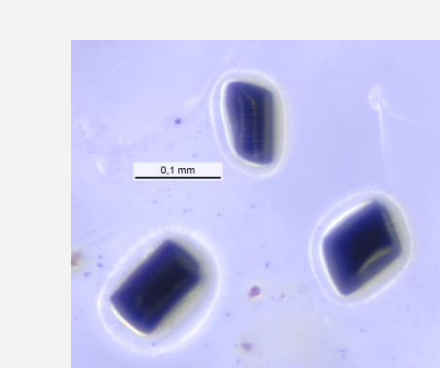
1) Solvent :  $\text{CH}_3\text{CN}/1.1.2 \text{ TCE } 11/1 \text{ mL}$

$T = 3^\circ \text{ C}$ ,  $I = 1$  to  $5 \mu\text{A}$

$\rightarrow$  2 PHASES IN THE SAME CELL



Prisms



Unit cell,  $T = 150 \text{ K}$ ,  $\lambda = 0.71073 \text{ \AA}$  :

$a = 7.9969(7) \text{ \AA}$   $\alpha = 77.707(9)^\circ$

$b = 11.072(1) \text{ \AA}$   $\beta = 75.377(7)^\circ$

$c = 13.171(1) \text{ \AA}$   $\gamma = 73.42(1)^\circ$

$V = 1068.9(2) \text{ \AA}^3$

$R1 = 3.70\%$

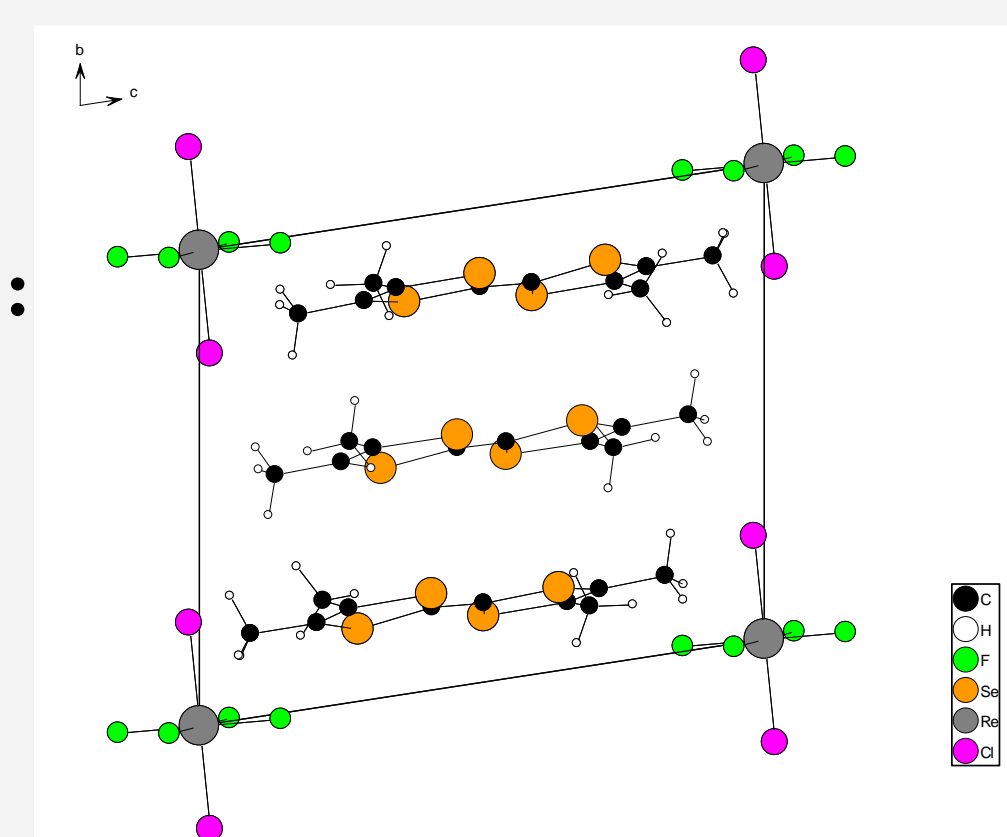
Triclinic system, P-1

$\text{Re}^{(\text{IV})}\text{-Hal}$  bond lengths ( $\text{ \AA}$ ) :

$\text{Re1-F(1)} \ 1.953(3)$

$\text{Re1-F(3)} \ 1.951(3)$

$\text{Re1-Cl(1)} \ 2.3183(2)$



Uniform stacking of oxydized TMTSeF molecules, isolated chains

+  $(\text{TMTSeF})_2\text{Re}^{(\text{V})}\text{F}_6$  : rhénium (IV) has been oxydized in rhénium (V)

Very small needles!

Unit cell,  $T = 150 \text{ K}$ ,  $\lambda = 0.71073 \text{ \AA}$

$a = 7.1590(8) \text{ \AA}$   $\alpha = 83.28(1)^\circ$

$b = 7.741(1) \text{ \AA}$   $\beta = 87.15(1)^\circ$

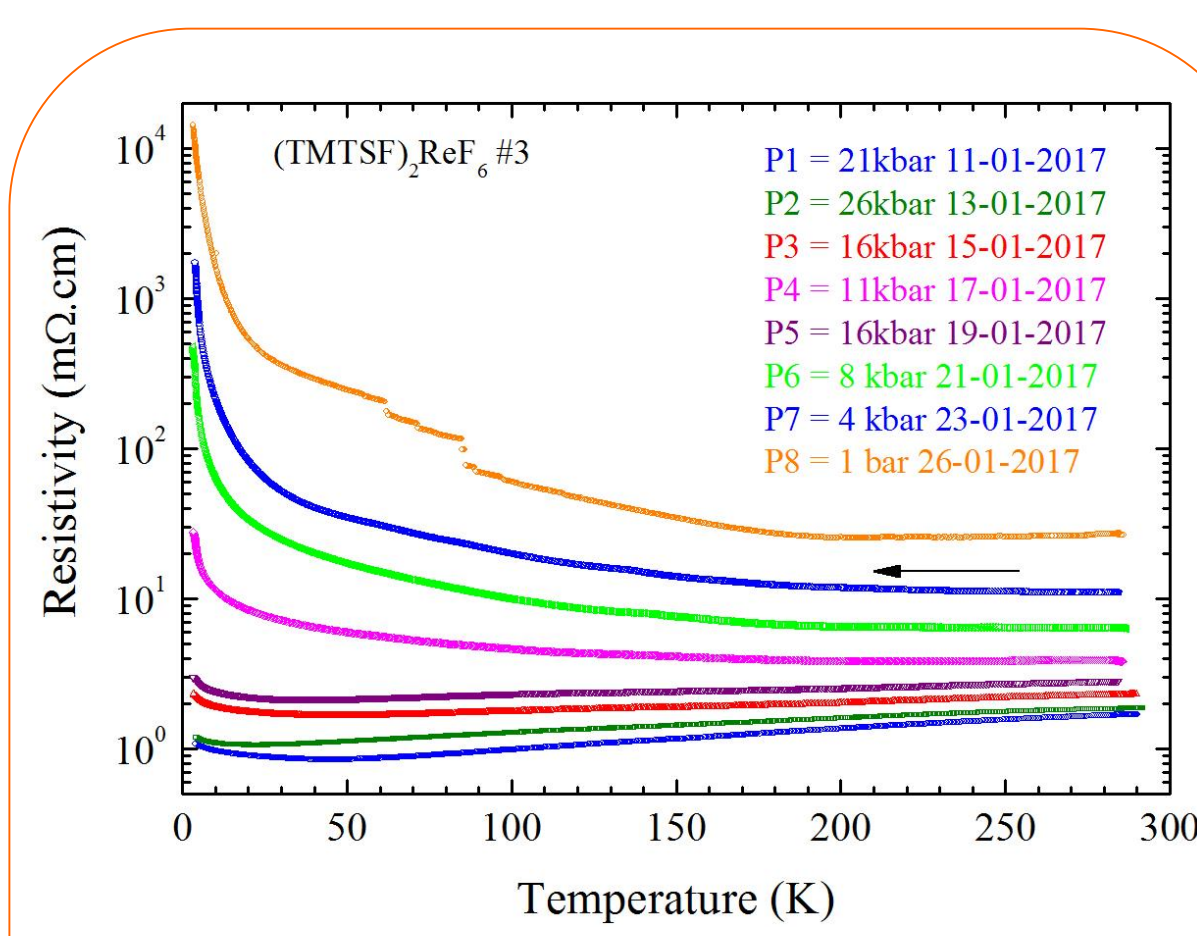
$c = 13.706(3) \text{ \AA}$   $\gamma = 70.19(1)^\circ$

$V = 709.7(2) \text{ \AA}^3$

$R1 = 2.63\%$

Triclinic, P-1

« Bechgaard » phase [3]



Resistivity (P. Auban Senzier)

$\text{Re}^{(\text{V})}\text{-F}$  bond lengths ( $\text{ \AA}$ )

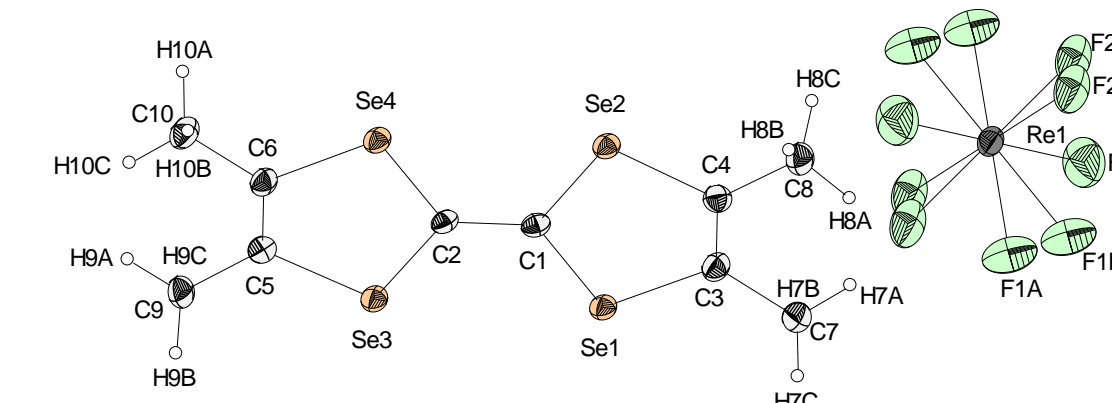
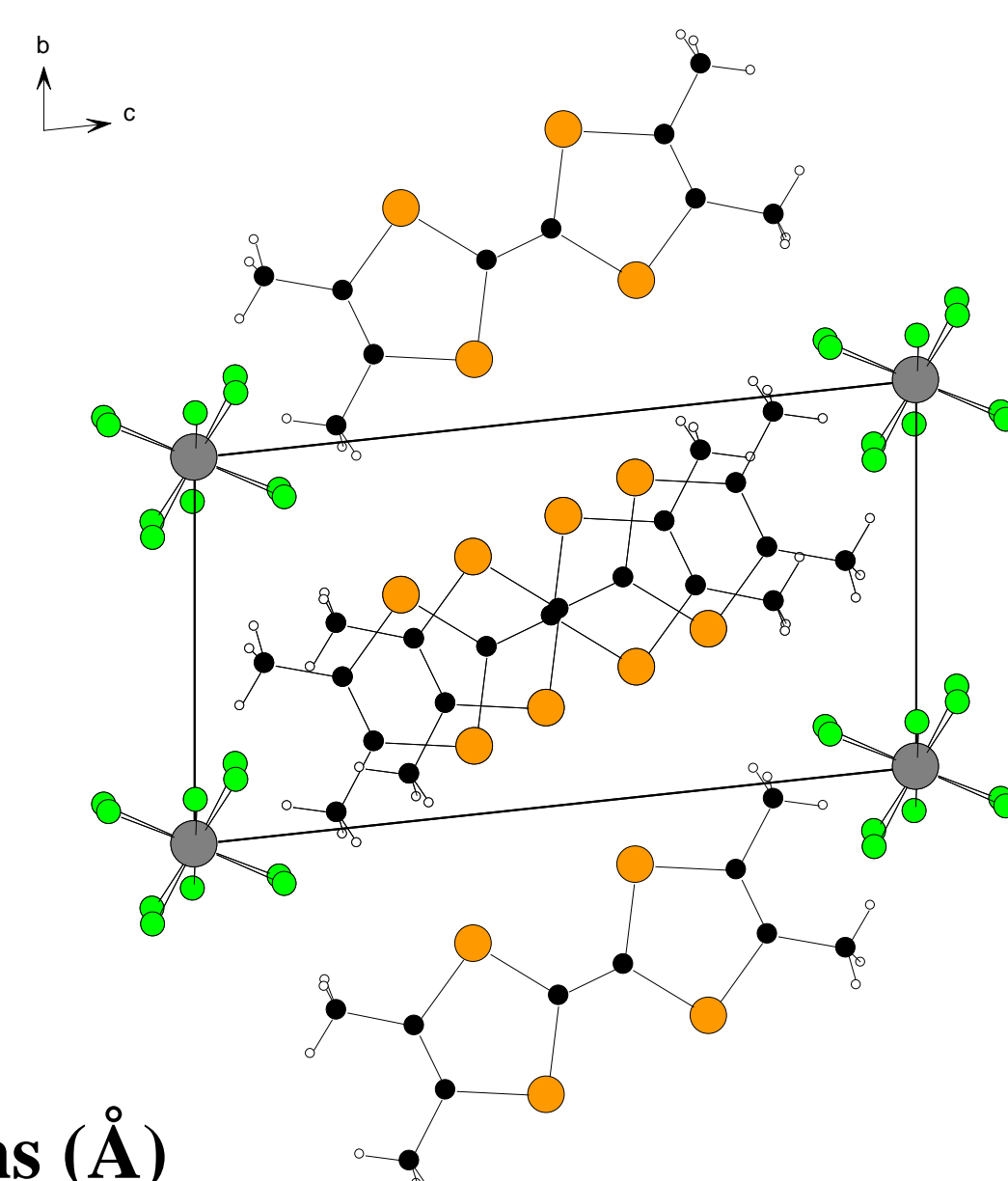
$\text{Re1-F(1A)} \ 1.875(3)$

$\text{Re1-F(1B)} \ 1.88(2)$

$\text{Re1-F(2A)} \ 1.889(3)$

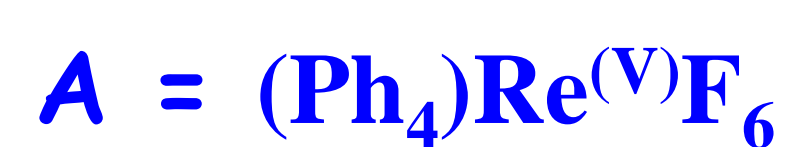
$\text{Re1-F(2B)} \ 1.796(18)$

$\text{Re1-F(3)} \ 1.870(3)$

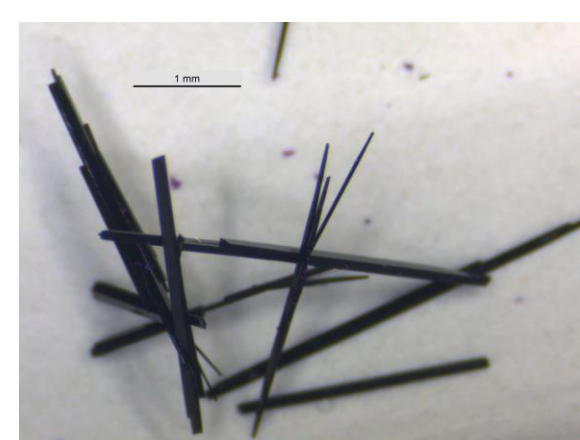


Unit cell at 100K : the disorder on F atoms disappears

Magnetism (R. Clérac) : measurements in progress



Larger needles



2) Solvent :  $\text{CH}_3\text{CN}/1.1.2 \text{ TCE } 11/1$

$T = 20^\circ \text{ C}$ ,  $I = 0.5 \mu\text{A}$

Only the  $(\text{TMTSeF})_2\text{Re}^{(\text{V})}\text{F}_6$  phase

Attempts to synthesize the  $(\text{TMTTF})_2\text{Re}^{(\text{V})}\text{F}_6$  salt : do not work, TMTTF is immediatly oxydized by  $\text{Re}^{(\text{V})}$

### $\text{A} = \text{TBATa}^{(\text{V})}\text{F}_6 \Rightarrow$ Diamagnetism/probe



Unit cell,  $T = 150 \text{ K}$ ,  $\lambda = 0.71073 \text{ \AA}$

$a = 7.7344(7) \text{ \AA}$   $\alpha = 92.376(5)^\circ$

$b = 10.8408(8) \text{ \AA}$   $\beta = 98.270(6)^\circ$

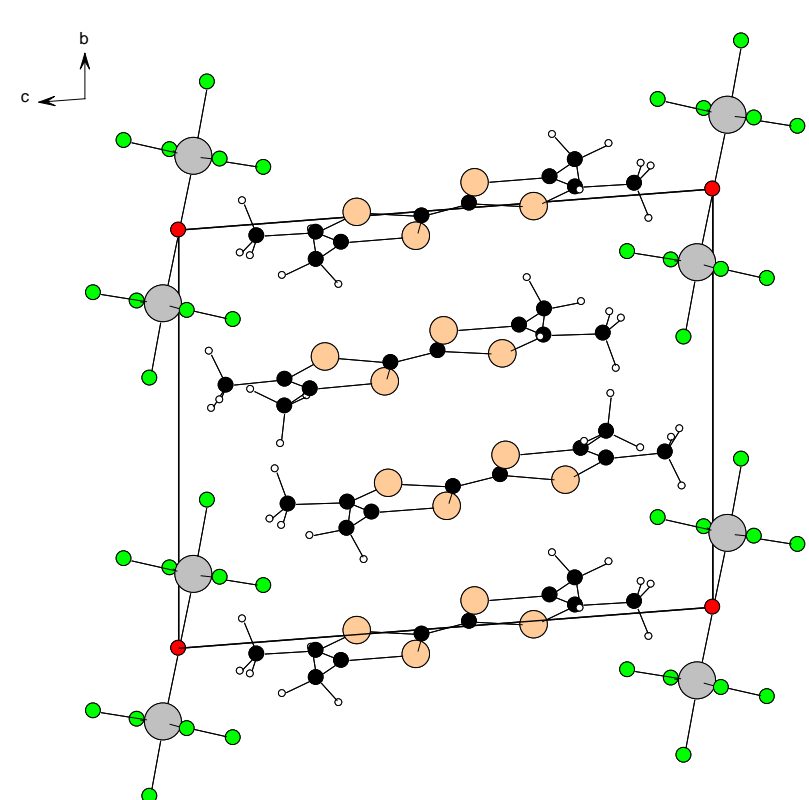
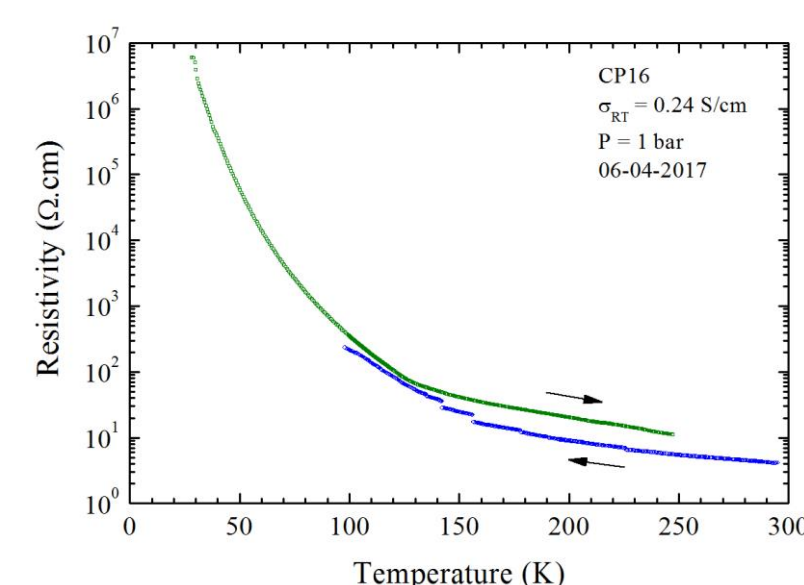
$c = 13.6409(9) \text{ \AA}$   $\gamma = 103.103(7)^\circ$

$V = 1099.13(15) \text{ \AA}^3$

$Z=1$ ,  $R1 = 4.39\%$

Triclinic system, P-1

Ref *Synth. Met.* 1991, 42, 1939-1942



$\text{TaF}_5 + \text{TBABF}_4 \rightarrow \text{TBATaF}_6$  [4]



$\text{Ta}^{(\text{V})}\text{-F}$  bond lengths ( $\text{ \AA}$ )

$\text{Ta1-F(1)} \ 1.892(3)$

$\text{Ta1-F(2)} \ 1.892(3)$

$\text{Ta1-F(3)} \ 1.895(3)$

Unit cell,  $T = 100 \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$

$a = 7.1344(4) \text{ \AA}$   $\alpha = 83.378(5)^\circ$

$b = 7.7255(5) \text{ \AA}$   $\beta = 87.118(5)^\circ$

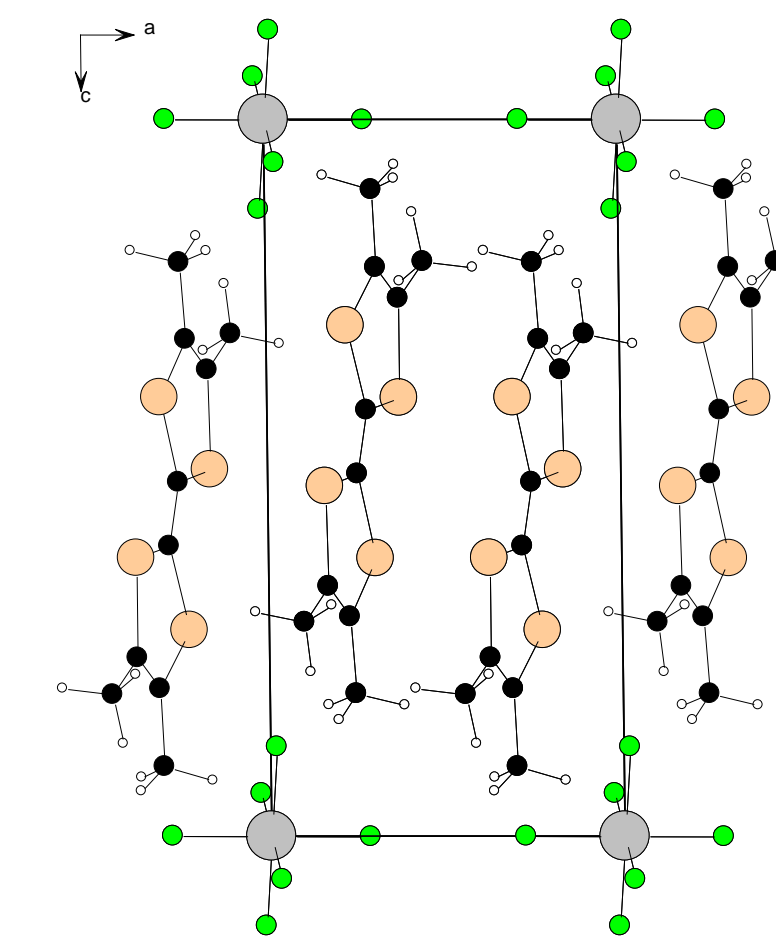
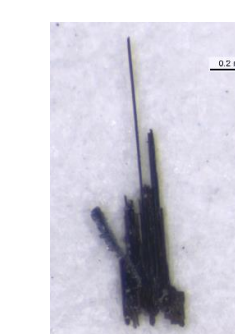
$c = 13.7204(9) \text{ \AA}$   $\gamma = 70.200(6)^\circ$

$V = 706.72(8) \text{ \AA}^3$

$Z=1$ ,  $R1 = 3.17\%$

Triclinic system, P-1

« Bechgaard » phase [3]



### Focus : pre oxydation of the $\text{Re}^{(\text{IV})}$ salt in situ

New  $(\text{TMTSeF})_2\text{ReO}_4$  phase = « Bechgaard » phase polymorph

$(\text{Ph}_3\text{-PNP-Ph}_3)_2 \text{Re}^{(\text{IV})}\text{F}_6(\text{H}_2\text{O})_x$  salt: 2 éq. mol  
Solvent :  $\text{CH}_3\text{CN}/1.1.2 \text{ TCE } 11/1$   
 $T = 20^\circ \text{ C}$ ,  $I = 10 \mu\text{A}$  during 5 days in order to oxydize 50% of the anion  
Then the TMTSeF is added in the anodic compartment and  $I = 2 \mu\text{A}$

Shiny platelets : too small for physics!



Like  $(\text{TMTSeF})_2\text{ClO}_4$  called «  $\mu$  » phase [5]

Unit cell,  $T = 150 \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$

$a = 11.7777(3) \text{ \AA}$

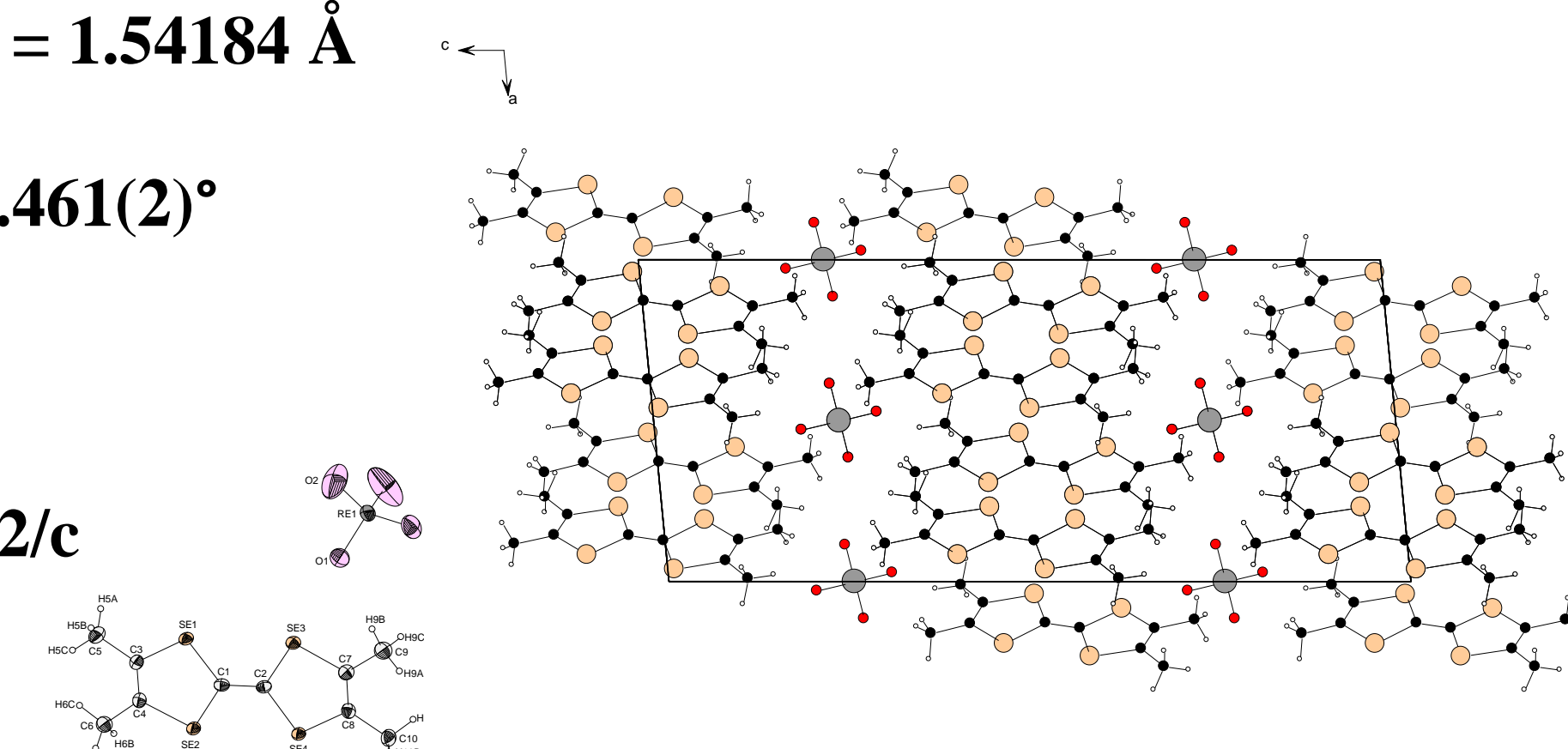
$b = 8.7928(2) \text{ \AA}$   $\beta = 95.461(2)^\circ$

$c = 27.0167(6) \text{ \AA}$

$V = 2785.12(11) \text{ \AA}^3$

$Z=4$ ,  $R1 = 2.52\%$

Monoclinic system, C 2/c



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[5] S. Perruchas, J. Fraxedas, E. Canadell, P. Auban-Senzier P. Batail, E. Canadell, *Adv. Mater.* 2005, 17, 209-212