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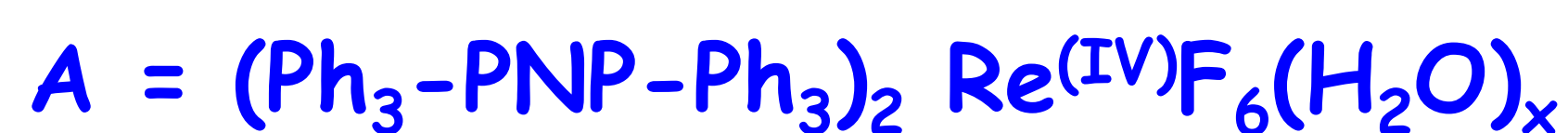
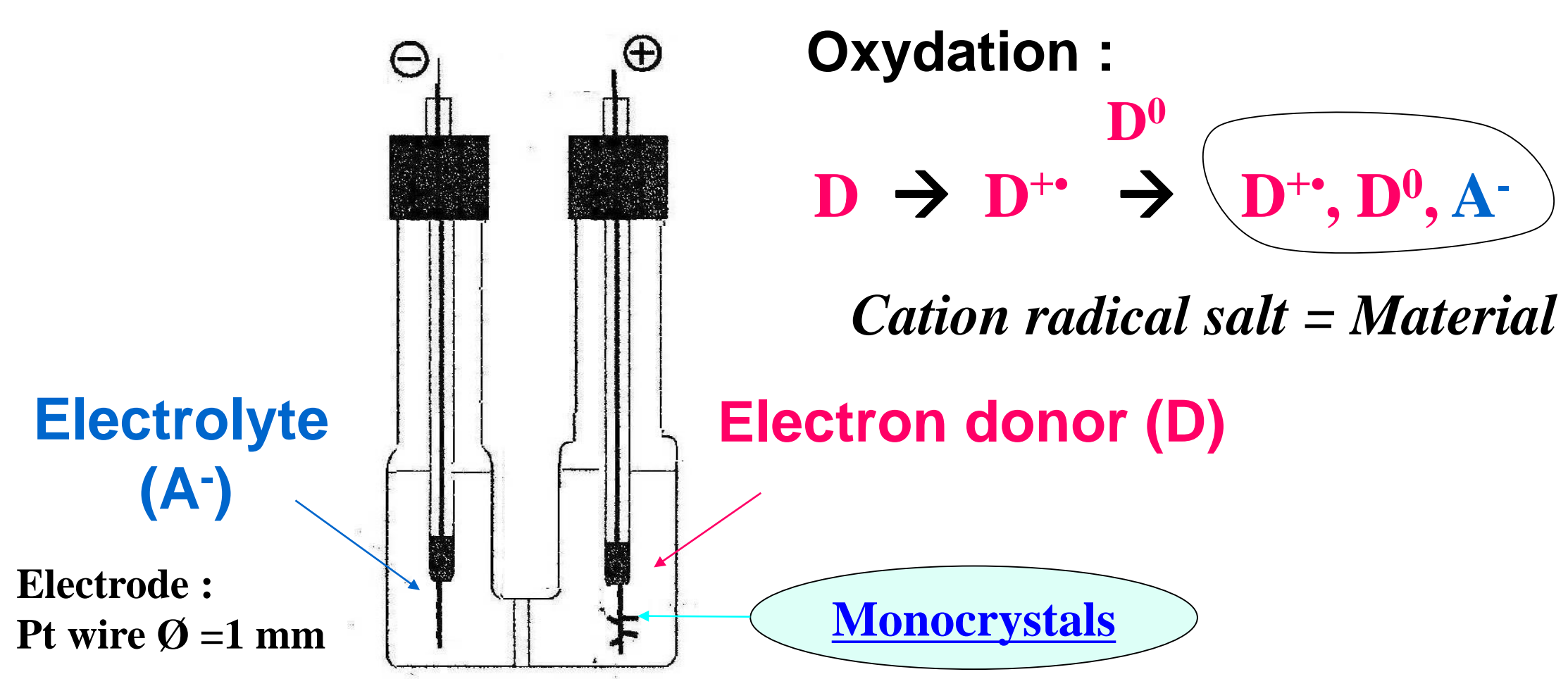
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Electrocrystallization set up [1]



TETRAMETHYL-TETRATHIAFULVALENE

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

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



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

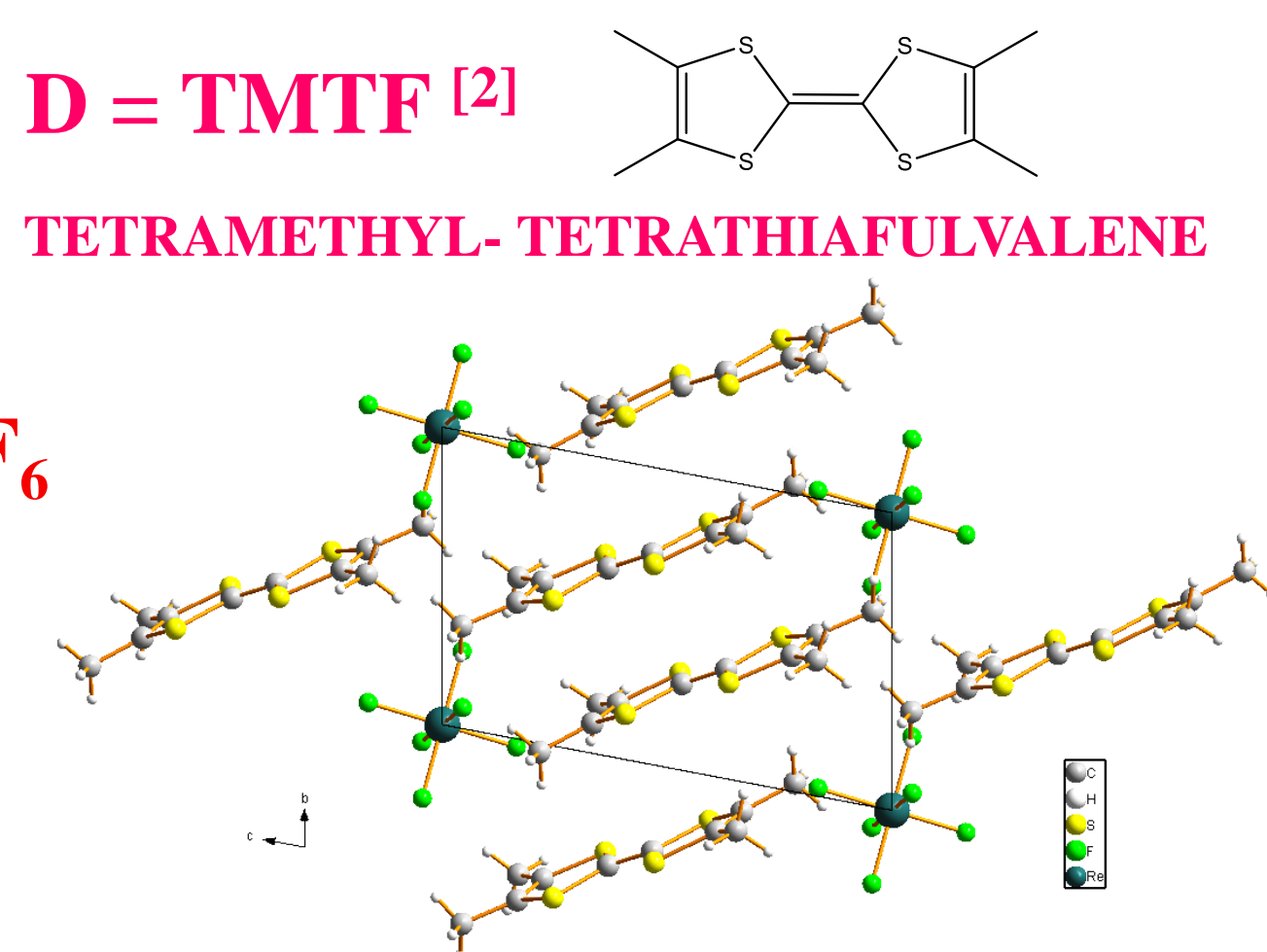
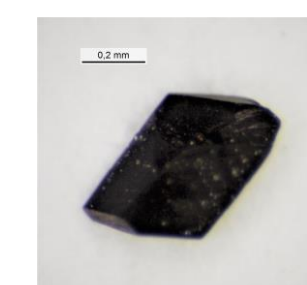
$a = 7.9941(17)\text{Å}$ $\alpha = 79.85(2)^\circ$

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

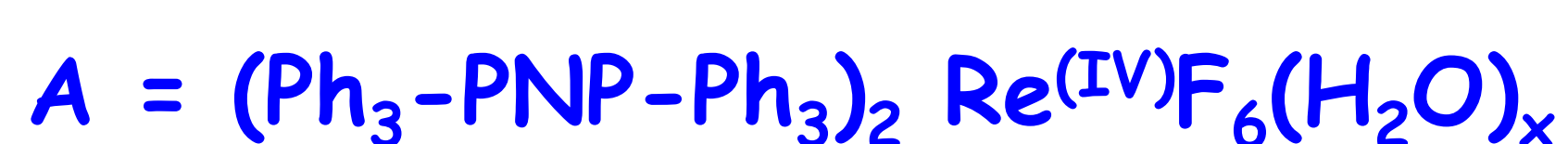
$c = 11.372(3)\text{Å}$ $\gamma = 65.466(18)^\circ$

$V = 659.71(30) \text{Å}^3$

Triclinic system, P-1



Strong dimerization \rightarrow insulating 1D system



TETRAMETHYL-TETRASELENAFULVALENE

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

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

\Rightarrow 2 PHASES IN THE SAME CELL



Prisms



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

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

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

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

$V = 1068.9(2) \text{Å}^3$

$R1 = 3.70\%$

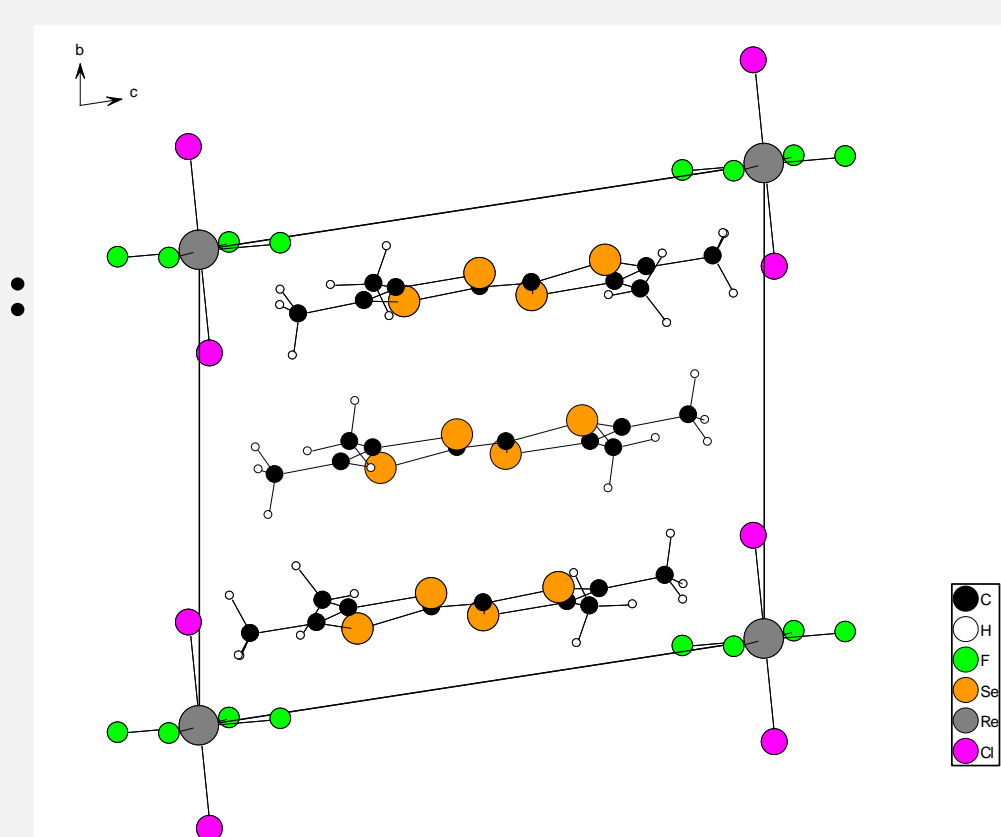
Triclinic system, P-1

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

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

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

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



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, $T = 150 \text{K}$, $\lambda = 0.71073 \text{Å}$

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

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

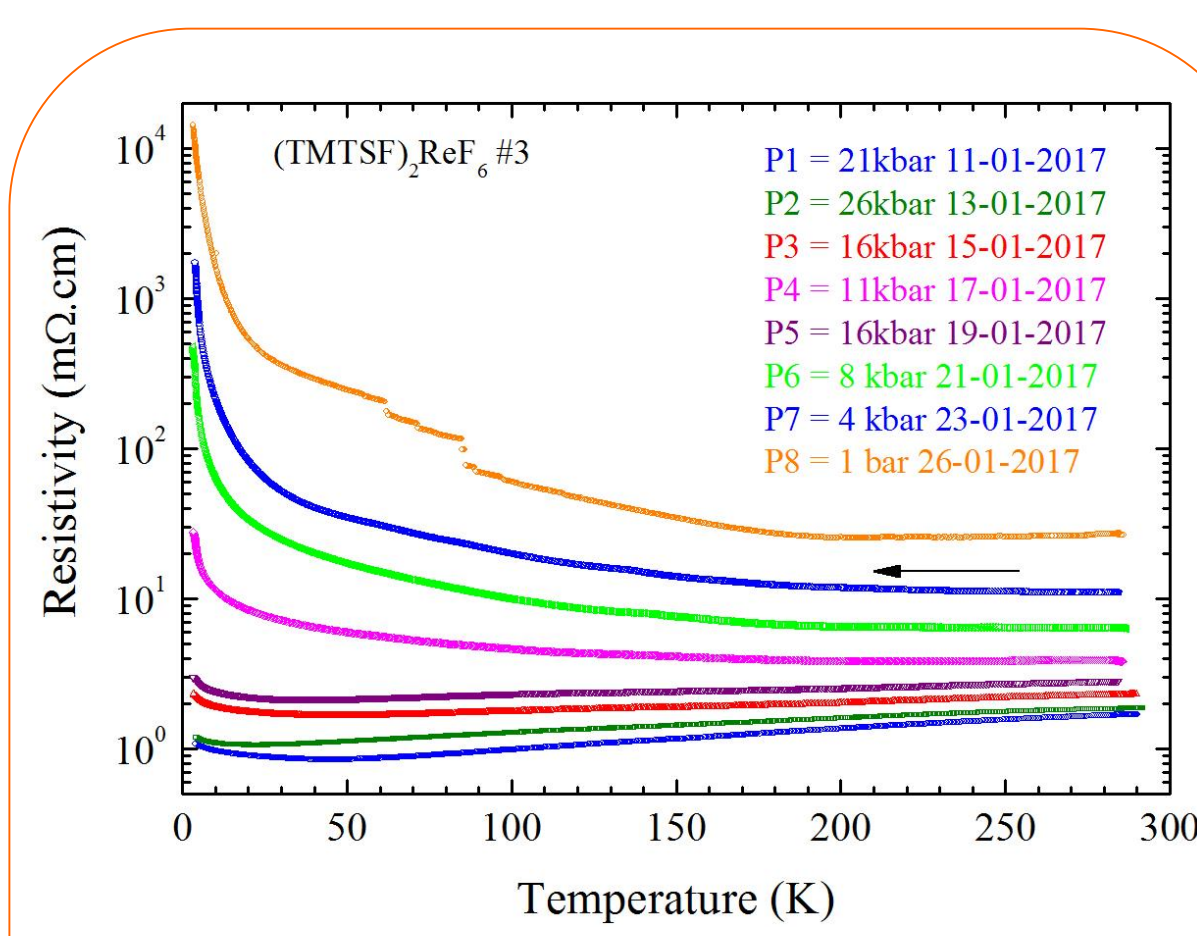
$c = 13.706(3)\text{Å}$ $\gamma = 70.19(1)^\circ$

$V = 709.7(2) \text{Å}^3$

$R1 = 2.63\%$

Triclinic, P-1

« Bechgaard » phase [3]



Resistivity (P. Auban Senzier)

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

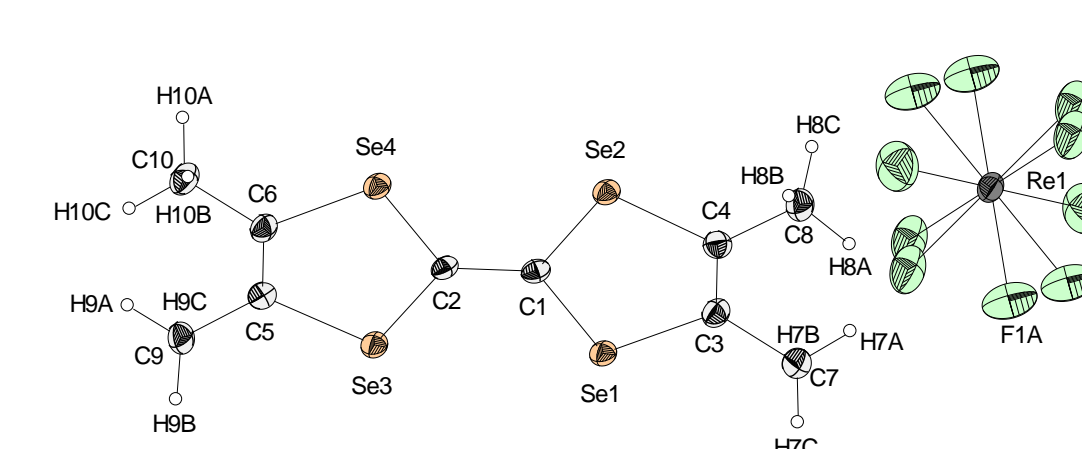
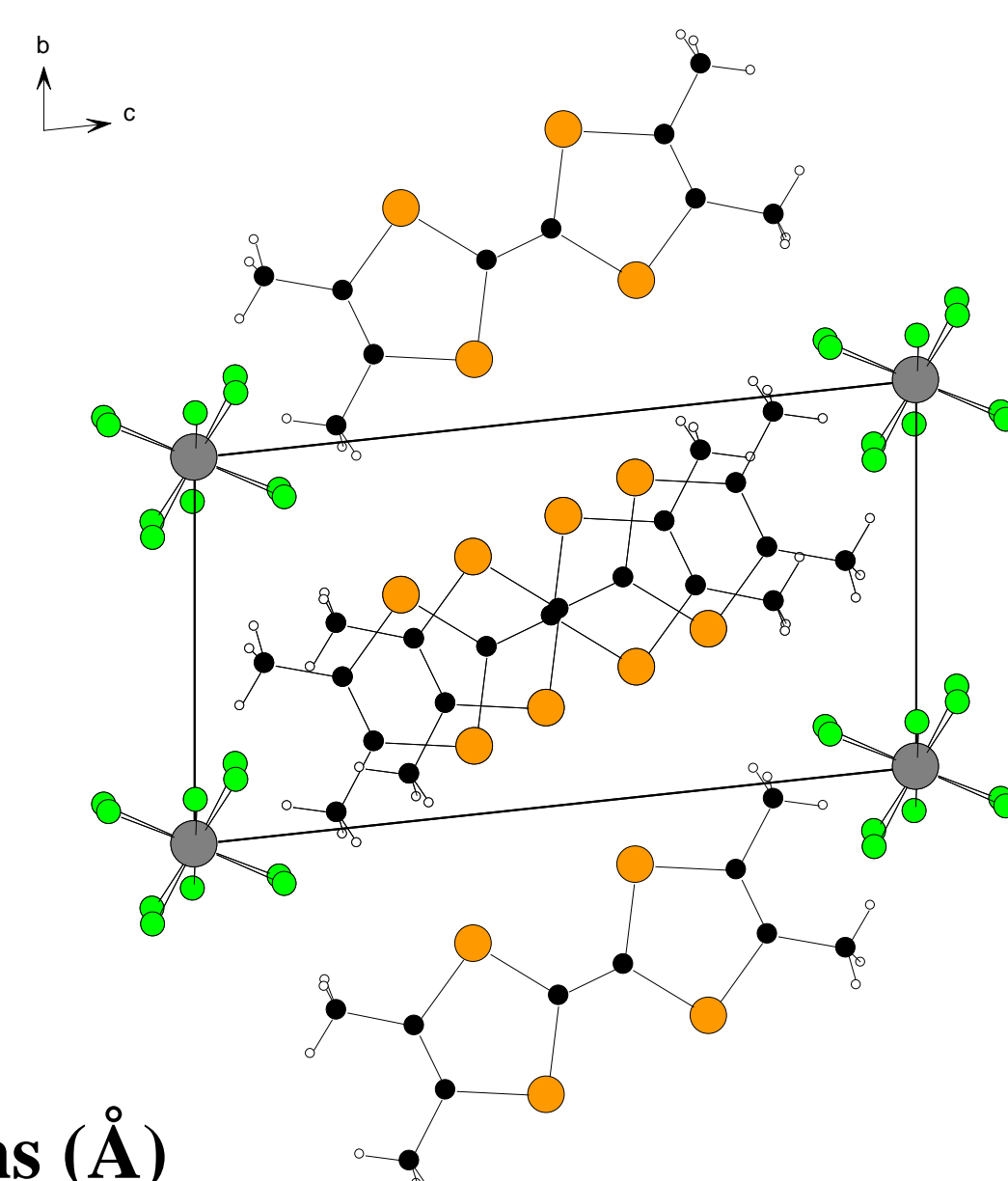
$\text{Re1-F(1A)} \quad 1.875(3)$

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

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

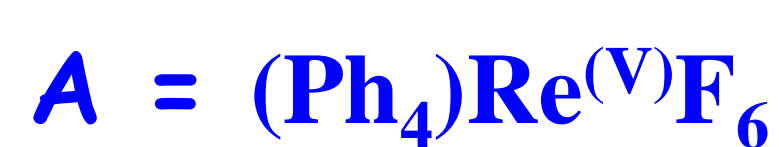
$\text{Re1-F(2B)} \quad 1.796(18)$

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

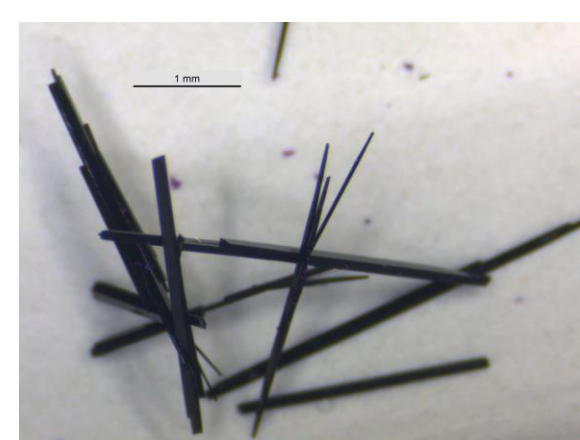


Unit cell at 100K : the disorder on F atoms disappears

Magnetism (R. Clérac) : measurements in progress



Larger needles



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

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

\Rightarrow 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, $T = 150 \text{K}$, $\lambda = 0.71073 \text{Å}$

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

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

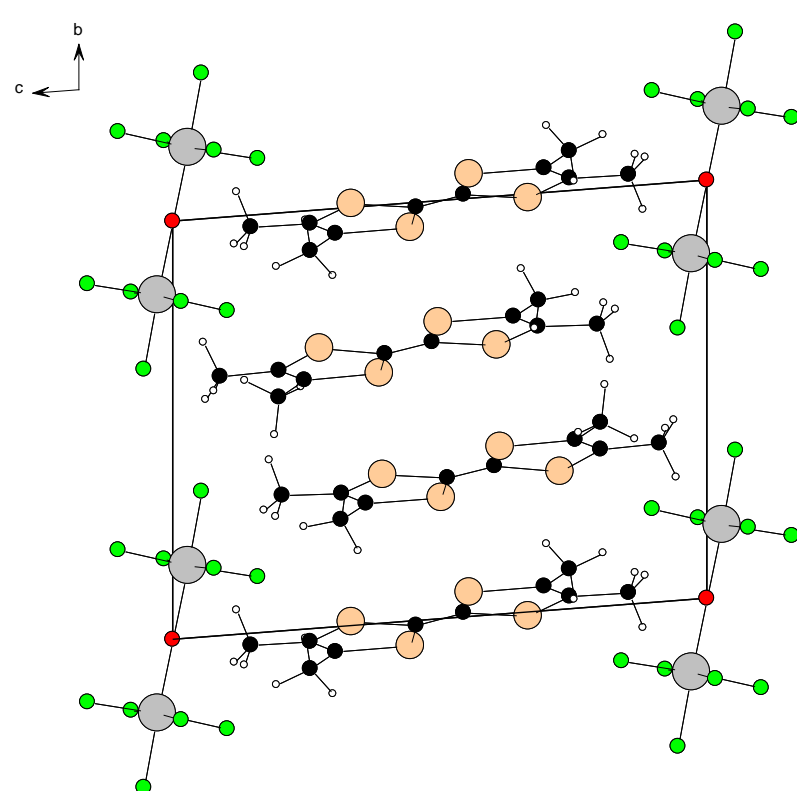
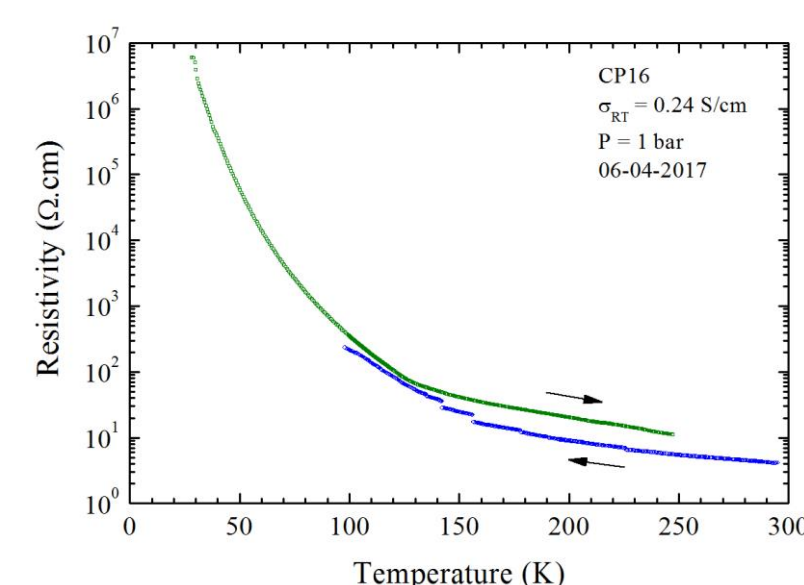
$c = 13.6409(9)\text{Å}$ $\gamma = 103.103(7)^\circ$

$V = 1099.13(15) \text{Å}^3$

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

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 (Å)

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

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

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

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

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

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

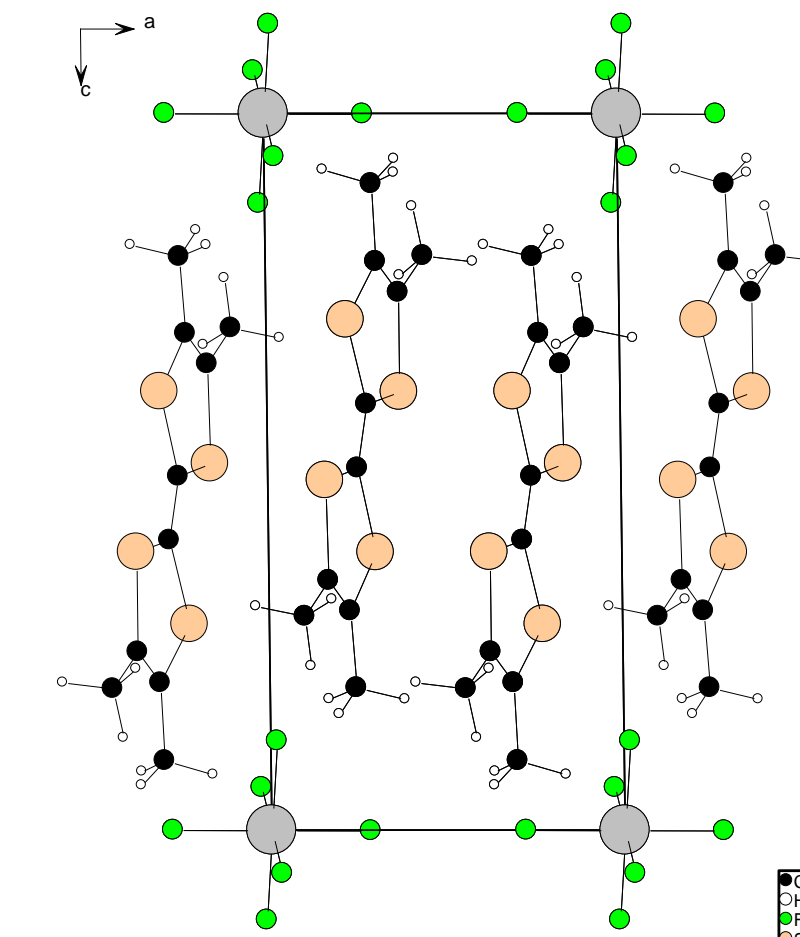
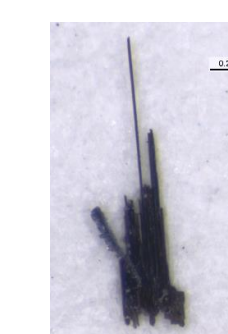
$c = 13.7204(9)\text{Å}$ $\gamma = 70.200(6)^\circ$

$V = 706.72(8) \text{Å}^3$

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

Triclinic system, P-1

« Bechgaard » phase [3]



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

\Rightarrow 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 : $\text{CH}_3\text{CN}/1.1.2$ 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 « μ » phase [5]

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

$a = 11.7777(3)\text{Å}$

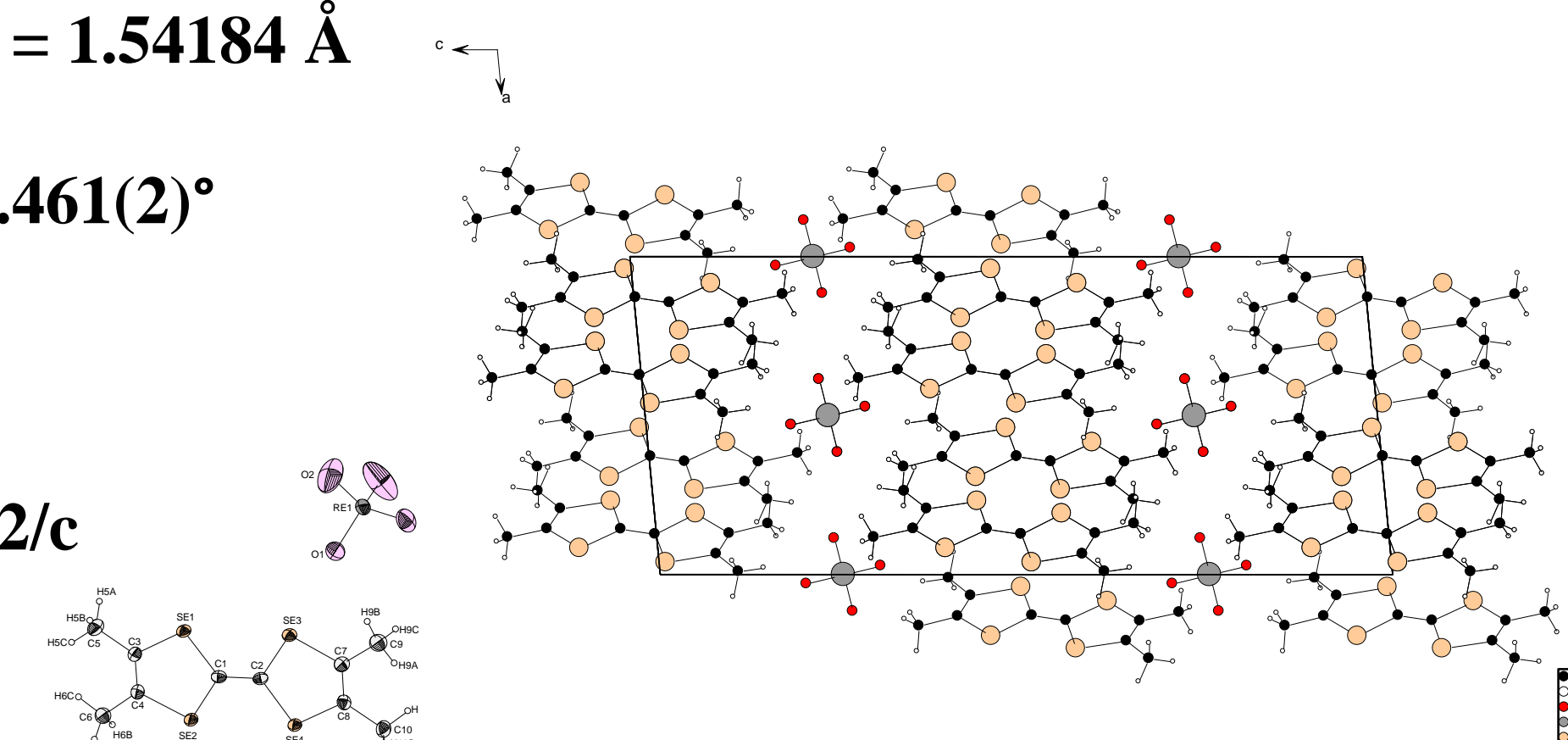
$b = 8.7928(2)\text{Å}$ $\beta = 95.461(2)^\circ$

$c = 27.0167(6)\text{Å}$

$V = 2785.12(11) \text{Å}^3$

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

Monoclinic system, C 2/c



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