



HAL
open science

UNUSUAL STOICHIOMETRY FOR NEW CONDUCTING ENANTIOPURE RADICAL CATION SALTS OF TM-BEDT-TTF WITH THE W6O19 2- DIANION

Cécile Mézière, Magali Allain, Flavia Pop, Pascale Auban Senzier, Narcis
Avarvari

► **To cite this version:**

Cécile Mézière, Magali Allain, Flavia Pop, Pascale Auban Senzier, Narcis Avarvari. UNUSUAL STOICHIOMETRY FOR NEW CONDUCTING ENANTIOPURE RADICAL CATION SALTS OF TM-BEDT-TTF WITH THE W6O19 2- DIANION. Journées Scientifiques régionales 2024 de la Société Chimique de France (SCF-BPL), Jun 2024, LOGONNA-DAOULAS (29), France. hal-04627316

HAL Id: hal-04627316

<https://hal.science/hal-04627316>

Submitted on 27 Jun 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

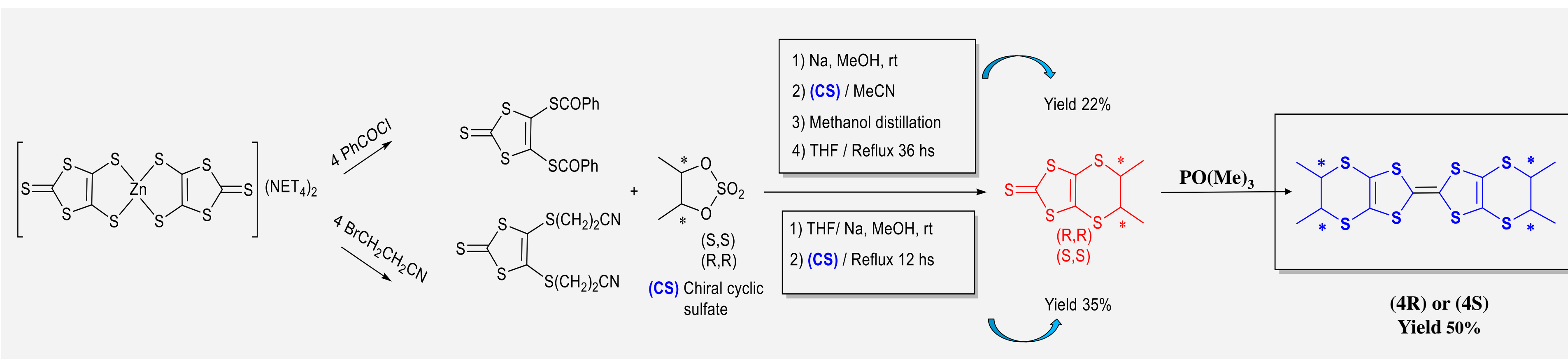
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cécile Mézière ¹, Magali Allain ¹, Flavia Pop ¹, Pascale Auban Senzier ² and Narcis Avarvari ¹

¹Laboratoire MOLTECH-Anjou, UMR 6200 CNRS-Université d'Angers, SFR Matrix, 2 bd Lavoisier, 49045 ANGERS Cedex, France

²Laboratoire de Physique des Solides, UMR8502 CNRS-Université Paris Sud, Bât. 510, 1 rue Nicolas Appert, 91405 Orsay Cedex, France

TM-BEDT-TTF synthesis



Chirality is introduced using chiral 2,3-butanediol for the preparation of the chiral cyclic sulphates (CCS) [1]

The synthesis of the chiral dimethyl thione has been optimised to avoid steps, reduce handling time and increase the yield

Chiral tetramethyl bis(ethylenedithio)-tetrathiafulvalenes are obtained by symmetric coupling in phosphite medium

Electrocrystallization set up [2]

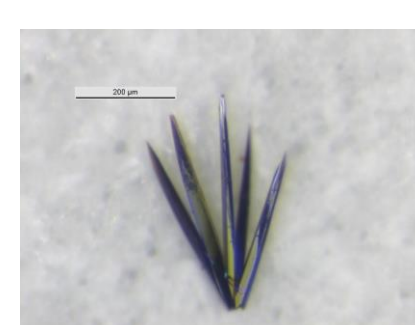
Background / Mo_6O_{19} dianion [3]

$(n-Bu_4N)_2Mo_6O_{19}$ synthesis: polymerisation of molybdic acid at $T < 50^\circ C$ in an acid medium^[4]: $6 Na_2MoO_4 + 10 HCl + 2 (n-Bu_4N)Br \rightarrow (n-Bu_4N)_2Mo_6O_{19} + 10 NaCl + 2 NaBr + 5 H_2O$

2:1 Phase (rac)-(TM-BEDT-TTF)₂Mo₆O₁₉

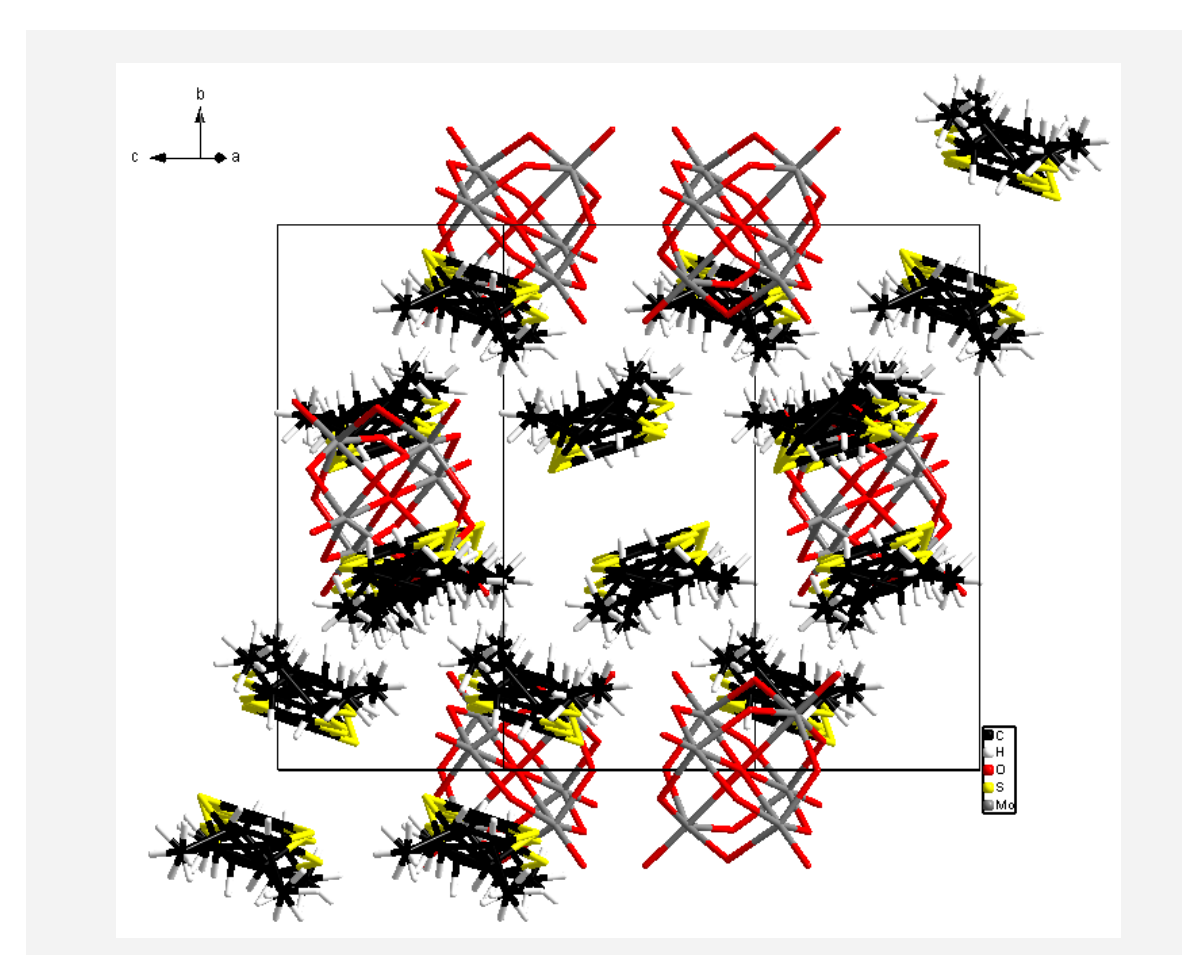
Solvent: Acetonitrile / Bromoform 50/50
T = 20 °C, I = 0.5 μA

9:5 Phase (4R) or (4S)-(TM-BEDT-TTF)₉(Mo₆O₁₉)₅(CHBr₃)_{8,67}



Black needles

Unit cell, T = 150 K, phase (rac)
Monoclinic system, $P 2_1/n$
a = 12.2033(2) Å α = 90°
b = 15.5932(2) Å β = 111.257(2)°
c = 13.9105(2) Å γ = 90°
V = 2466.91(7) Å³
Z = 2, R1 = 4.39 %

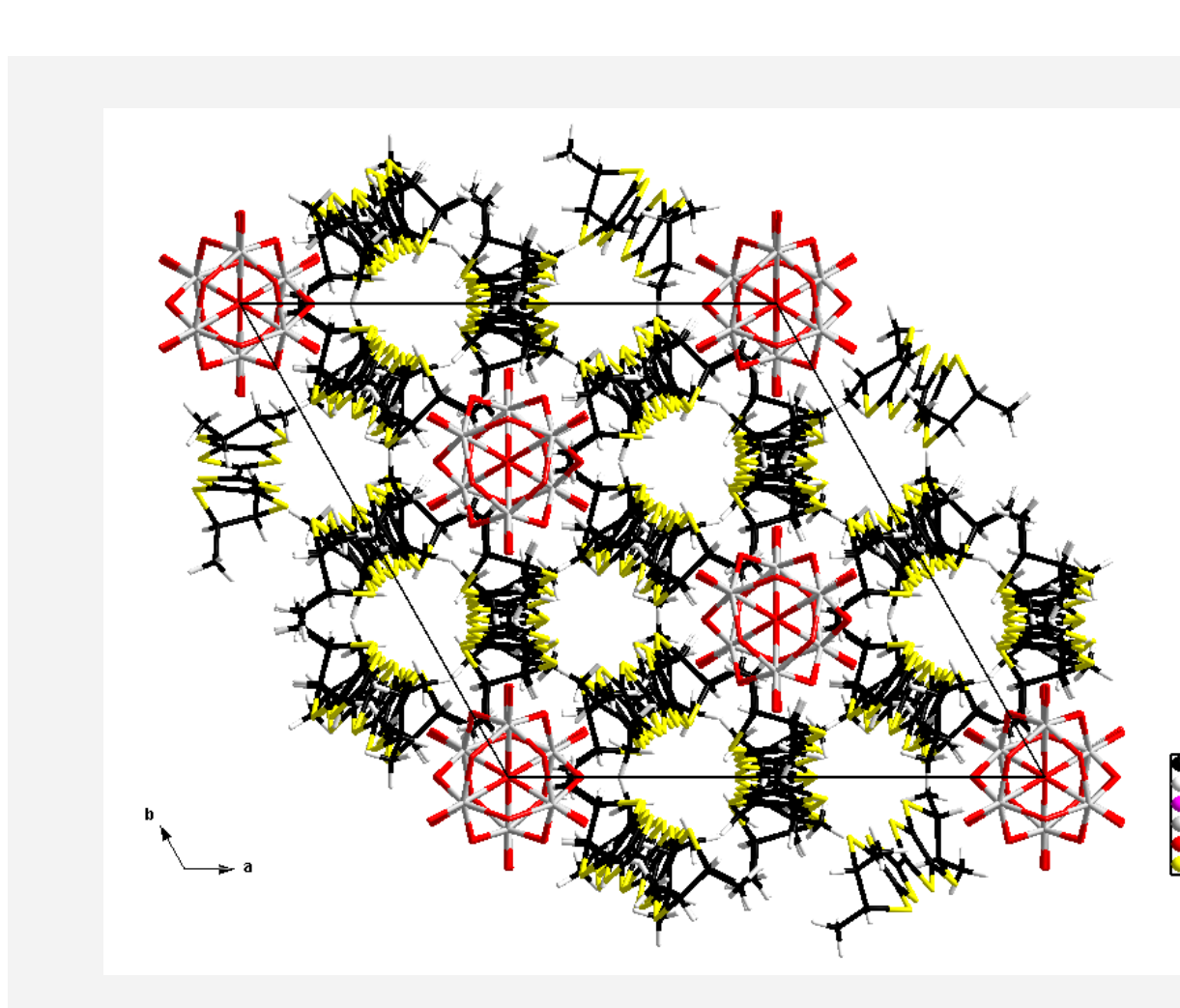
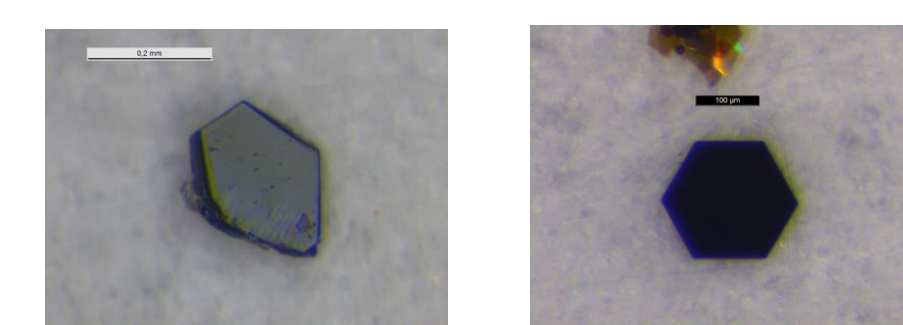


Strong dimers

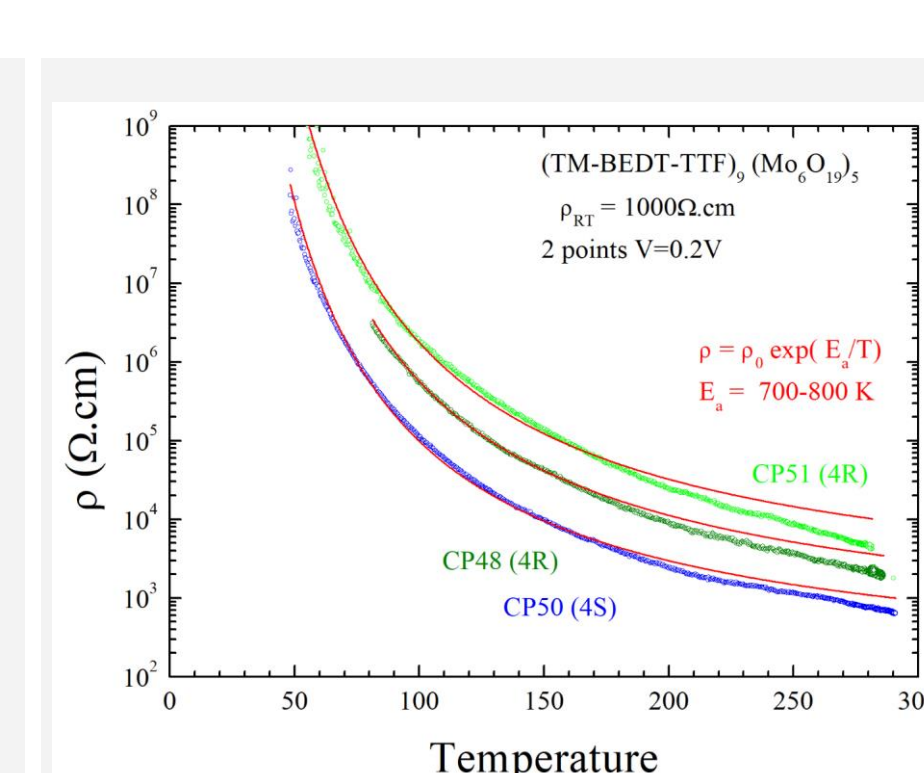
⇒ Ionic charge stoichiometry / Insulating materials

Black hexagonal platelets

Unit cell, T = 150 K, phase (4R)
Trigonal system, R 3 2
a = 19.6963(4) Å α = 90°
b = 19.6963(4) Å β = 90°
c = 62.6651(13) Å γ = 120°
V = 21053.6(10) Å³
Z = 3, R1 = 7.65 %



Helical packing

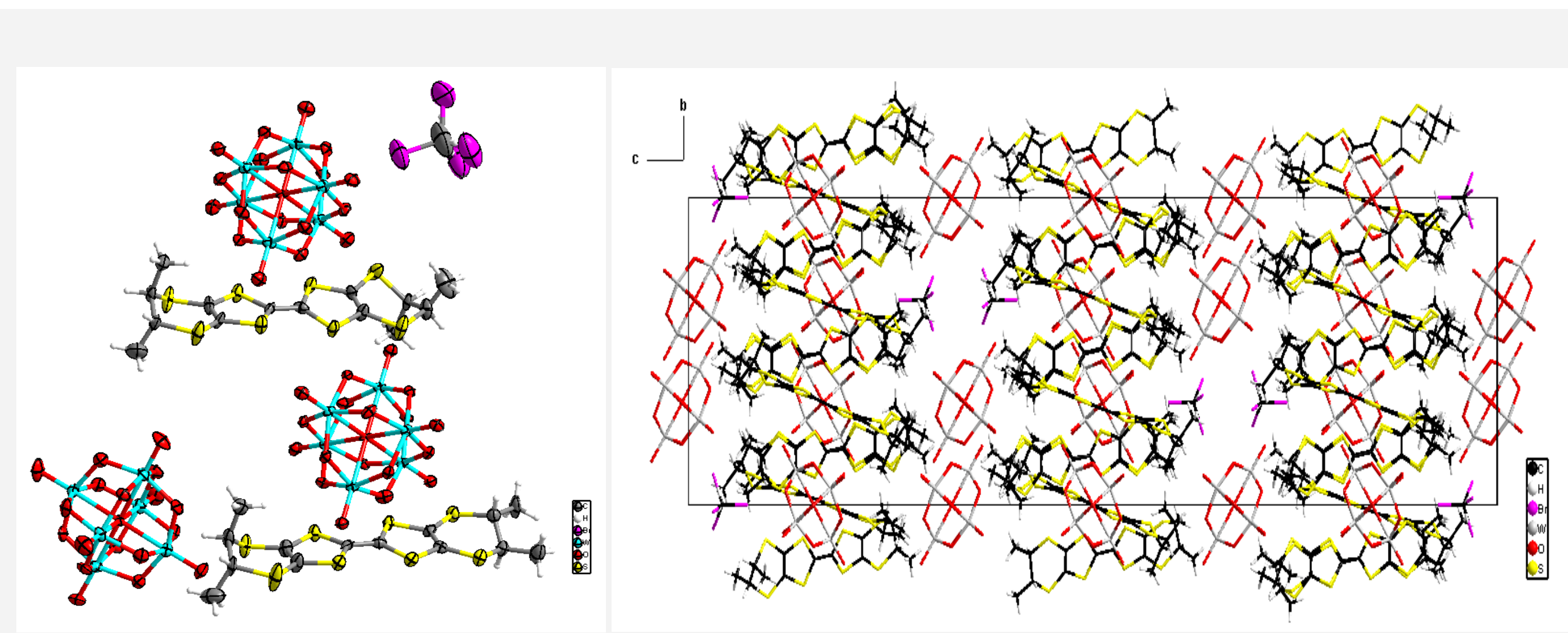


$\sigma_{RT} = 1,2 S/cm$

⇒ Semi-conducting materials

Latest developments with the W_6O_{19} dianion

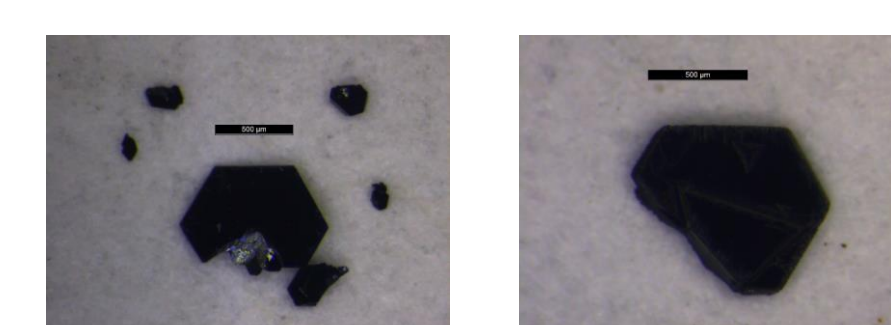
$(n-Bu_4N)_2W_6O_{19}$ synthesis: hot polymerisation of tungstic acid in an acid medium^[5]: $6 Na_2WO_4 + 10 HCl + 2 (n-Bu_4N)Br \xrightarrow{100^\circ C} (n-Bu_4N)_2W_6O_{19} + 10 NaCl + 2 NaBr + 5 H_2O$



The crystalline structure of the material is the same as the molybdenum equivalent

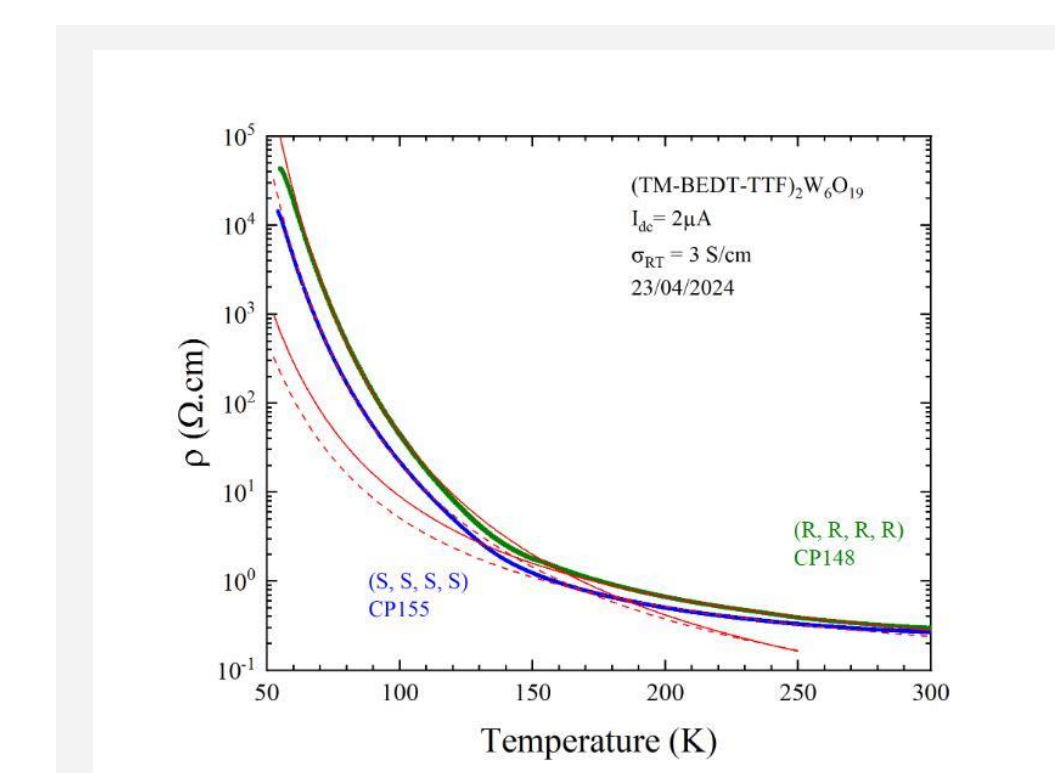
The 2:1 Phase (4R) or (4S)-(TM-BEDT-TTF)₂W₆O₁₉ is also present, in the shape of black needles

⇒ 9:5 Phase (4R) or (4S)-(TM-BEDT-TTF)₉(W₆O₁₉)₅(CHBr₃)₈



Black hexagonal platelets

Unit cell, T = 200 K, phase (4R)
Trigonal system, R 3 2
a = 19.7950(4) Å α = 90°
b = 19.7950(4) Å β = 90°
c = 62.6851(9) Å γ = 120°
V = 21271.9(9) Å³
Z = 3, R1 = 4.69 %



$\sigma_{RT} = 3 S/cm$

The W₆O₁₉ salt is more conductive

⇒ Prospects: measuring conductivity under pressure

+ chiral magnetic effect (Geert Rikken LNCMI)

[1] F. Pop, P. Auban-Senzier, A. Frąckowiak, K. Ptaszyński, I. Olejniczak, J. D. Wallis, E. Canadell, N. Avarvari, *J. Am. Chem. Soc.* 2013, 135, 45, 17176

[2] P. Batail, K. Boubekour, M. Fourmigué, J. C. Gabriel, *Chem. Mater.*, 1998, 10, 3005

[3] F. Pop, C. Mézière, M. Allain, P. Auban-Senzier, N. Tajima, D. Hirobe, H. M. Yamamoto, E. Canadell, N. Avarvari, *J. Mater. Chem. C*, 2021, 9, 10777

[4] M. Che, M. Fournier, J. P. Launay, *J. Chem. Phys.*, 1979, 71, 1954

[5] *Inorganic Synthesis*, volume 27, Wiley Interscience Publication, 1990, 80