EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structural Analysis of Organic Spin Ladder Systems	**Experiment number:** HC-918
Beamline: ID 11	**Date of experiment:** from: 23 Out 2013 to: 25 Out 2013	**Date of report:**
Shifts: 6	**Local contact(s):** Jonathan Paul Wright (email: wright@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Manuel ALMEIDA*, Dr Isabel SANTOS*, Rafaela SILVA*, Instituto Tecnológico e Nuclear, Portugal

Report:

The main goal of the proposal which was the determination of the low temperature (T<220K) structure of the molecular spin ladder system **$(DT\text{-}TTF)_2[Cu(mnt)_2]$** was fully achieved by the structural refinement of the data containg the weak asatellite refelections corresponding to the lattice doubling along the chain direction (*b*) below 220K.

The structural refinement celarly shows that the dimerisation , denoted by rather weak superlattice reflections, is associated with charge ordering leading to an alternation of neutral and radical cation donors, along the chain axis as shown in fig 1. The neutral and cationic donor molecules are clearly denoted by different bond lenghts. These results are presently under publication.

$(DT\text{-}TTF)_2[Cu(mnt)_2]$	Prev. work	Aver. ESRF	Full ESRF
T (K)	293(2)	120	120
Sp.Gr.	$P2_1/n$	$P2_1/n$	P-1
a [Å]	16.2990(5)	16.2478(19)	7.8686(6)
b [Å]	3.9079(3)	3.8767(4)	17.0085(12)
c [Å]	27.3225(17)	27.034(3)	27.555(2)
α [°]	90.000(5)	90.00	78.618(3)
β [°]	102.141(5)	101.693(2)	89.931(2)
γ [°]	90.000(5)	90.00	76.638(3)
V [Å^3]	1701(2)	1667.48	3513.56

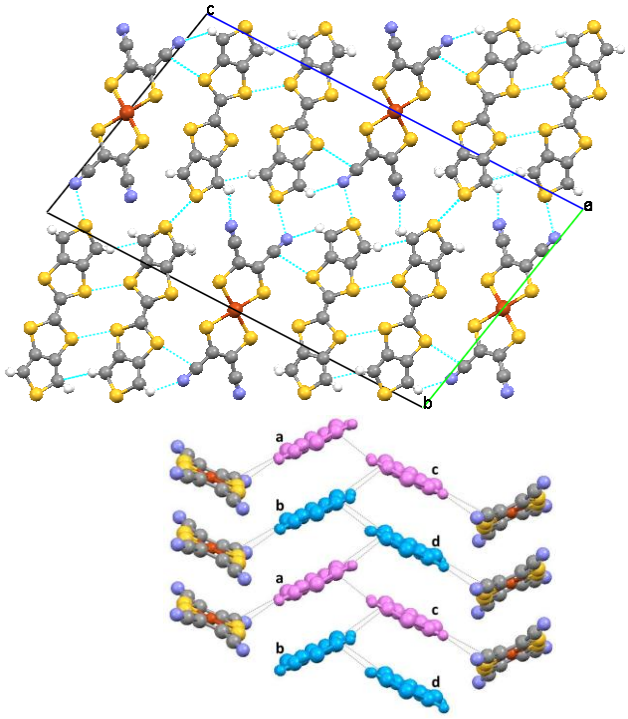
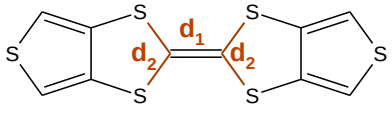


Fig 1- $(DT)_2[Cu(mnt)_2]$ structure viewed along chain axis (top) and side view of the donor double chains with charge alternation between neutral(b,d) and cationic (a,c) molecules.



	d_1	d_2				$<d_2>$
a	1,416(3)	1,764(2)	1,768(2)	1,764(2)	1,768(2)	1,766
b	1,380(3)	1,788(2)	1,795(3)	1,793(3)	1,798(2)	1,794
c	1,411(3)	1,774(2)	1,764(3)	1,769(3)	1,762(2)	1,767
d	1,389(3)	1,791(3)	1,796(2)	1,793(2)	1,791(3)	1,793

At ESRF line ID11 it was also possible collect data and solve the structure of the closely related compounds (α-DT-TTF)$_2$[Co(mnt)$_2$] and (α-mDT-TTF)[Co(mnt)$_2$] using small single crystals, below the size that can be measured in conventional laboratory diffractometers. Both compounds present dimerised anions. In first compound this dimerization appears however disordered with the Co atom distributed over two possible positions and with lack of correlation between the dimerization in nearby anionic chains. The structure is closely related with spin-ladder compound previously mentioned, but with a slightly different molecular packing with donors almost perpendicular to the stacking axis. These results are presently under publication.

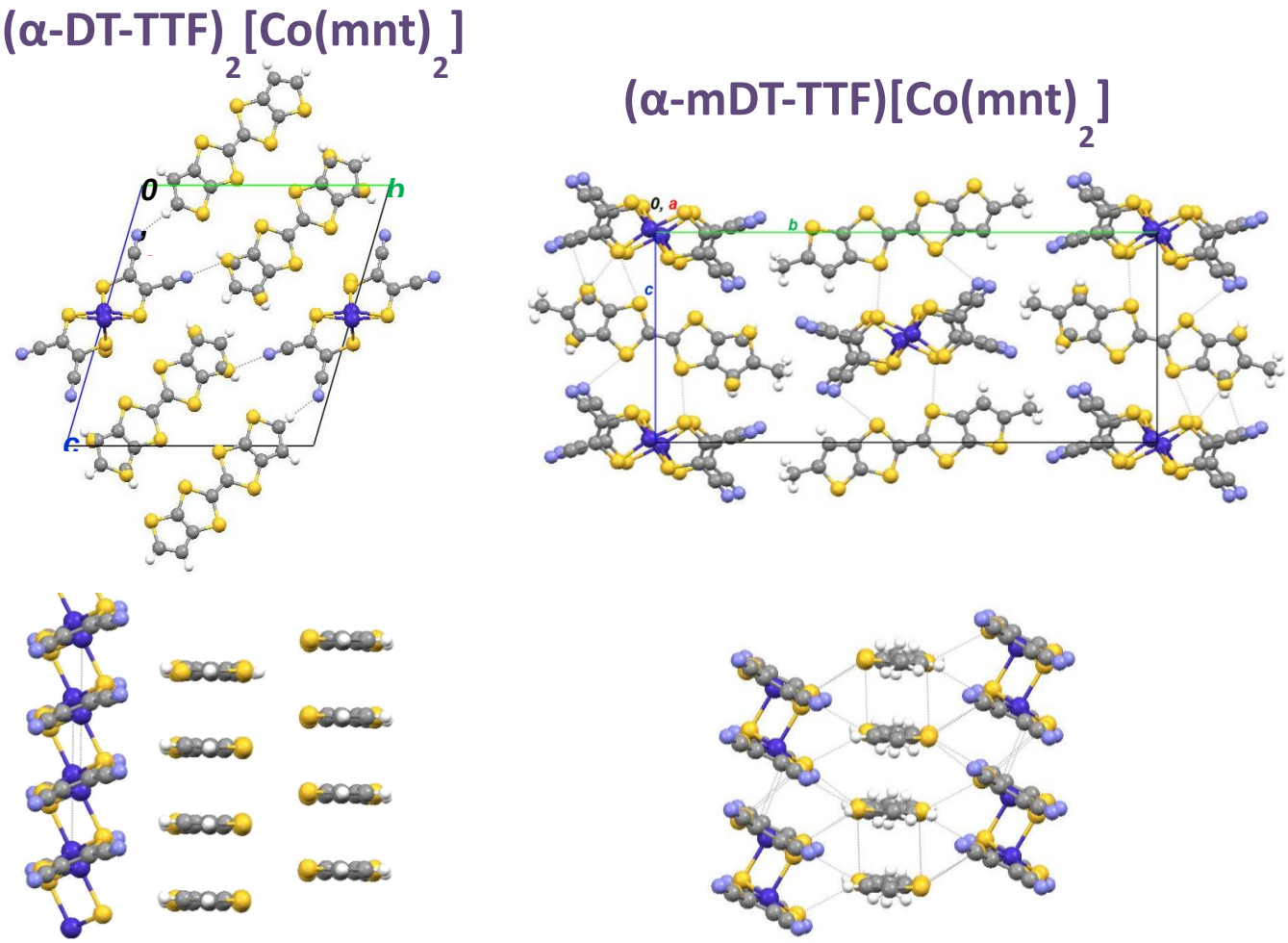


Fig. 2- Crystal structures of (α-DT-TTF)$_2$[Co(mnt)$_2$] (left) and (α-mDT-TTF)[Co(mnt)$_2$] (right).

Summary of crystal data.

Compound	(α-DT-TTF)$_2$[Co(mnt)$_2$]	(α-mDT-TTF)[Co(mnt)$_2$]
Formula	$C_{28}H_8CoN_4S_{16}$	$C_{40}H_{16}Co_2N_8S_{20}$
Space Group	P-1	P 2_1/c
a (Å)	3.8387(5)	7.4463(6)
b (Å)	15.543(4)	28.2680(14)
c (Å)	16.061(3)	12.2998(11)
α (º)	106.831(7)	90.00
β (º)	92.574(4)	99.825(2)
γ (º)	96.508(6)	90.00
Volume (Å^3)	908.269	2551.04
Z	1	2
R-Factor (%)	8.41	5.33