



Experiment title:

Structural analysis of (PER)₂[M(mnt)₂] compounds
M=Fe, Co and low temperature distortions

Experiment number:

HS-4500

Beamline:

ID11

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9

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Report:

The structure of the (Per)₂[M(mnt)₂] compounds M=Fe, Co was investigated at temperatures above and below the metal-insulator phase transitions which occur at 58 and 73 K respectively. These compounds are known to have an average structure corresponding to the so called β-phases type which for other transition metals is P₂/n with parameters a=17.5 Å, b=4.06 Å, c=25.03 Å, β=92.016(1)°. X-ray diffraction studies with laboratorial sources previously detected for the M=Fe and Co compounds a few centred unit cells with at least one parameter doubled; (b≈8.15 Å) and eventually also c=50.0 Å (see Fig 1 below). However a structural refinement for any of these compounds could never be made on the basis of this larger unit cells.

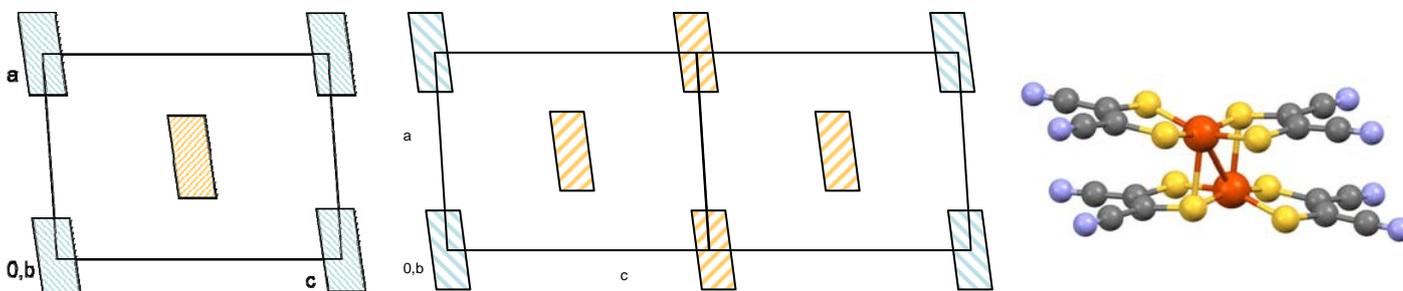


Fig 1- Left: Two unit cells for (Per)₂[M(mnt)₂], M=Fe, Co, with different anionic dimerisation phase arrangements, where the two anionic dimerised phases are depicted in different colours. Right: Anion dimer.

At ESRF line ID11 it was possible to collect data and solve the structure for both M=Co and Fe at 100 K on the basis of a triclinic cell depicted on left with parameters a≈25.0 Å, b≈8.0 Å, c≈17.0 Å, β=92 with dimerised anions, as shown in fig 1 right, in defined positions. The exact cell parameters are on table 1.

Table 1- Crystallographic data for Per₂[M(mnt)₂].

M	Fe	Co
Formula	C ₈₀ H ₄₈ FeN ₄ S ₄	C ₈₀ H ₄₈ CoN ₄ S ₄
Space Group	P-1	P-1
a (Å)	7,982	7,958
b (Å)	17,256	17,243
c (Å)	24,869	24,531
α (°)	91,990	92,06
β (°)	99,250	89,98
γ (°)	90,02	90,04
Volume (Å ³)	3378,75	3363,96
Z	2	2

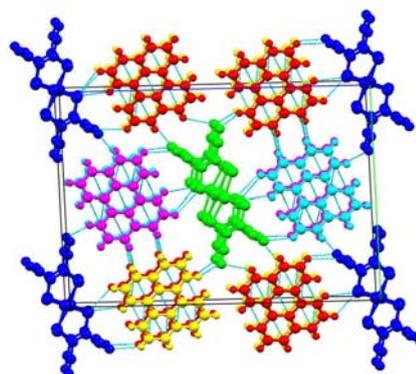


Fig 2- Per₂[Fe(mnt)₂] crystal structure viewed along a.

The structures of Fe and Co compounds are very similar and their refinement showed that the doubling of the unit cell corresponds to an arrangement of dimerised anions with alternated phases in nearby columns. In spite of some limitations in the quality of the refinement the results clearly show for the first time how the arrangement of the anion dimerisation implies a loss of symmetry in the donor chains that become unequivocal, with slightly rotated molecules.

The attempts to collect data below the M-I transitions, where an additional doubling of the unit cell parameter b with $b \approx 16$ Å is expected to occur, were complicated with problems of ice formation with the helium flow cryostat. Anyway data collected at 40K on both compounds failed to detect any additional spots corresponding to the parameter $b \approx 16.0$ Å, which are expected to be very small, at least one order of magnitude smaller than previous spots. These results are presently under publication.

In addition to these perylene compounds it was also investigated the structure of small single crystals of the charge transfer salts based on the donor α -DT-TTF with PF_6^- anion. In this compound, besides one monoclinic structure is $P2_1/c$, it was found an additional structural type with a triclinic unit cell, P-1, with parameters $a = 6.1471(16)$ Å, $b = 6.8439(19)$ Å, $c = 15.273(4)$ Å, $\alpha = 80.160(5)^\circ$, $\beta = 81.534(4)^\circ$, $\gamma = 80.559(5)^\circ$, $V = 619.8(3)$ Å³, $Z = 2$. The structural refinement in spite of limitations with the quality of data collected at synchrotron is entirely consistent with a structure similar to that of $(\text{BET-TTF})_2\text{PF}_6$ salt.

In the first structure the α -DT-TTF donors are in a trans conformation and regularly stacked at 3.511 Å intermolecular spacing along b , with their long axis approximately along a and tilted 23.7° towards the stacking b -axis (Fig. 3 left). The donor stacks are arranged side by side along c with alternating tilting angles towards b and in such a way that in the b,c plane there is a 2D network of short S...S contacts (Fig. 3b left). The donor layer alternate with layers of the PF_6^- anions which appear disordered in channels between the donors. In the unit cell, in a channel between four donor stacks there are two closely spaced (1.935 Å) phosphorus positions, with a reduced occupation factor of 0.3 and 8 partially occupied fluorine positions, (Fig. 3d left), corresponding to the stoichiometry $(\alpha\text{-DT-TTF})(\text{PF}_6)_{0.6}$. This is a clear sign of disorder in the PF_6^- anions and an indication that minor variations of the anion concentration are possible in this structure. The second structure reveals an almost regular stacking of donor molecules along a and an exact stoichiometry with anions in defined positions. These data were already published (R. A. L. Silva, *et al. Eur. J. Inorg. Chem.* 2013 in press DOI: 10.1002/ejic.201201362).

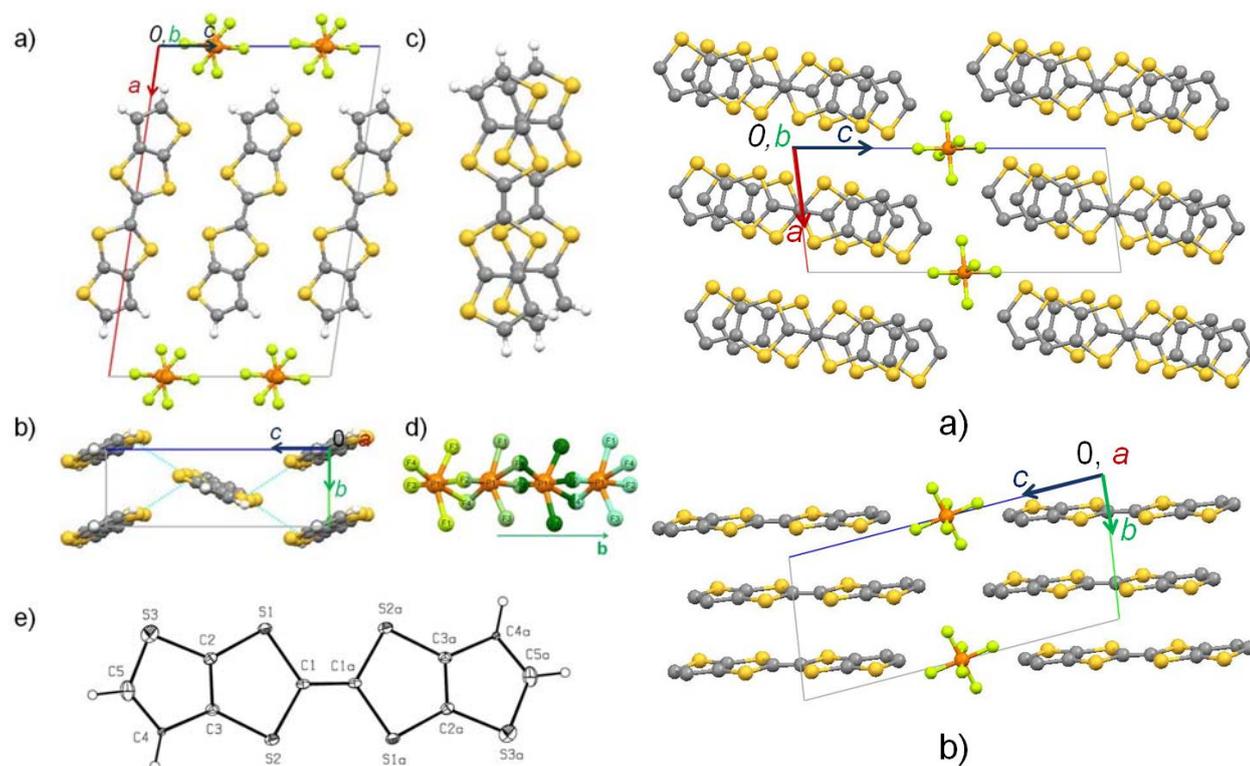


Figure 3- Left. $(\alpha\text{-DT-TTF})(\text{PF}_6)_{0.6}$ crystal structure: a) view along the b axis ; b) partial view of the donor layers along a axis; c) overlap mode of α -DT-TTF units; d) positions of disordered PF_6^- anions; e) ORTEP and atomic numbering scheme of the α -DT-TTF units (symm. op. $-x, -y, -z$) Right. Crystal structure of $(\alpha\text{-DTTF})_2\text{PF}_6$ viewed along b (top) and a (bottom).