ESRF	**Experiment title:** Crystal Structure of the First Organic /Inorganic Material Formed by the Electron Donor Bis(ethylenendithio)tetrathiafulvalene and the Ferromagnetic Polyoxometalate Cluster $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$	**Experiment number**: CH-897
Beamline: BM01A	**Date of experiment**: from: 15/11/2000 to: 20/11/2000	**Date of report**: 30 Aug 2001
Shifts: 15	**Local contact(s)**: Dr. Silvia Capelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The design and synthesis of molecular materials combining two or more physical properties as conducting, magnetic and optical is a contemporary challenge in the chemistry of materials. Our approach to this goal is to make two-network solids by combining magnetic polyoxometalates with partially oxidized organic π-electron donor molecules.[1]
The aim of the proposed experiment was to determine the crystal structure of the radical salt formed by the organic donor bis(ethylenedithio)tetrathiafulvalene and the inorganic polyoxometalate $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ which contains a ferromagnetic cluster. Several crystals of this compound were tested in the KUMA KM6-CH diffractometer but all of them were very weakly diffracting despite the use of synchrotron radiation and they did not produce diffraction of enough quality to abord a structural resolution.
It was then decided to test other conducting radical salts which belong to the same family of polyoxometalate-based molecular materials and being very related to the title compound. These salts contain the organic π-donor molecule bis(ethylenedioxo)tetrathiafulvalene or BEDO (Fig. 1) and the perylene (per) donor molecule (Fig. 2), combined with a polyoxometalate cluster with the so-called Keggin structure (Fig. 3). Previous attempts to collect data from these crystals in a conventional diffractometer equipped with MoKα radiation had been unsuccesful due to the small size of the crystals. In this case, the use of synchrotron radiation allowed the collection of diffraction data of enough quality and the crystal structures of both radical salts have been already solved. The compounds are formulated as $BEDO_6K_2[BW_{12}O_{40}]\cdot 8H_2O$ and $per_6[PMo_{12}O_{40}]\cdot CH_2Cl_2$. Their refined unit cells

were *a* = 11.728(2), *b* = 11.948(2), *c* = 23.335(5), α = 90.13(3), β = 102.20(3), γ = 117.43(3), V = 2817.9(2) and *a* = 14.059(3), *b* = 14.270(3), *c* = 27.053(5), α = 88.27(3), β = 86.65(3), γ = 86.02(3), V = 5403.2(3), respectively. The refinements were performed in the space group P-1 for both compounds and final values of R1 = 0.0949, wR2 = 0.2447 (for 13468 unique reflections, 727 parameters and 26 restraints) and R1 = 0.0773, wR2 = 0.2566 (for 966 parameters and 113 restraints) have been reached for the compounds $BEDO_6K_2[BW_{12}O_{40}]\cdot 8H_2O$ and $per_6[PMo_{12}O_{40}]\cdot CH_2Cl_2$ respectively.

The crystal structure of the radical salt $BEDO_6K_2[BW_{12}O_{40}]\cdot 8H_2O$ consists of alternated layers of the organic donors and the inorganic polyoxometalates (Fig. 4) while the structure of $per_6[PMo_{12}O_{40}]\cdot CH_2Cl_2$ is made of chains of perylene molecules which form channels in which the polyoxometalates and other isolated perylene molecules accomodate (Fig. 5).

These two compounds represent the first radical salts of polyoxometalate clusters combined with BEDO and perylene donors. The structural resolution will allow us to understand the conducting behaviour of these radical salts (the BEDO compound is metallic, while the perylene salt is semiconducting).

Two publications are being prepared with these results.

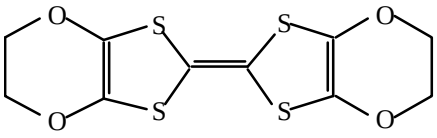


Figure 1

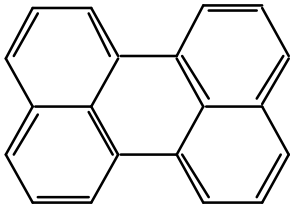
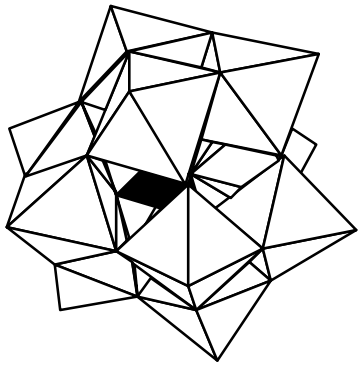


Figure 2



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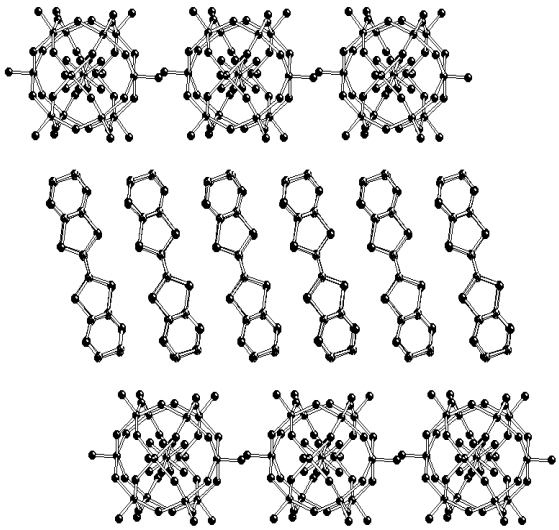

Figure 4

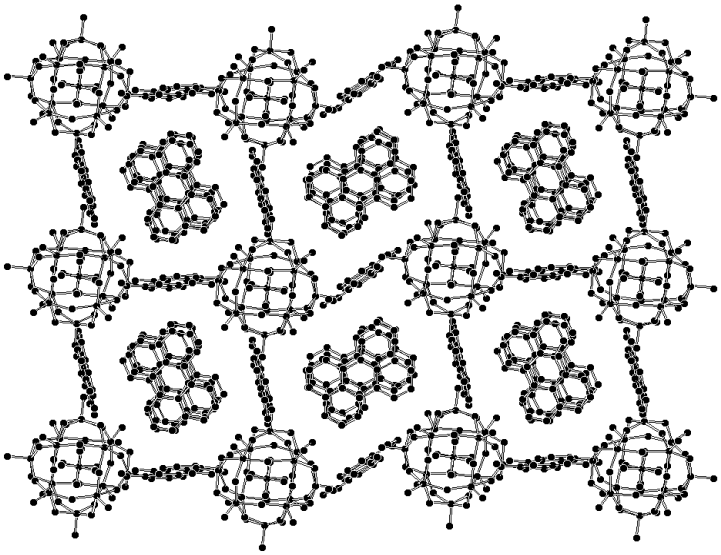

Figure 5

References:

1 – (a) Coronado, E. and Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273-296 and references therein.
(b) Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J. and Triki, S. *J. Am. Chem. Soc.* **1998**, *120*, 4671-4681.