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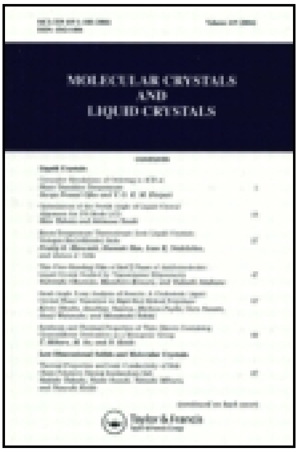

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$(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ and $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$: Two New Examples of 1D Organic Antiferromagnetic Systems

C. Bellitto [a], M. Bcnamico [a] & G. Stauio [a]

[a] I. T. S. E., C. N. R., Area della Ricerca di Roma, C. P. 10, Via Salaria Km. 29. 5, 00016, Monterotondo Staz., Italy

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$(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ AND $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$: TWO NEW EXAMPLES OF 1D ORGANIC ANTIFERROMAGNETIC SYSTEMS.

C. BELLITTO, M. BONAMICO, and G. STAULO.
I.T.S.E., C.N.R., Area della Ricerca di Roma, C.P. 10, Via Salaria Km.29.5, 00016 Monterotondo Staz., Italy.

Abstract. $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$ has been characterized by *EPR*, *UV-visible*, *IR* spectroscopy and by static magnetic susceptibility. It contains the mixed-valence paramagnetic anion $[PMo_{12}O_{40}]^{4-}$ and the BEDT-TTF molecules are ionised with an average degree of charge ρ=+0.5. The compound is isomorphous with $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$, the crystal structure of which is known. The magnetic properties of both salts have been studied. They are highly localised, low-dimensional spin S=1/2 systems, with one spin per BEDT-TTF dimer.

INTRODUCTION

Low-dimensional charge-transfer salts based on organic donors with small closed-shell anions have been studied in detail[1], while those with large inorganic clusters are not well developed [2,3,4]. Our interest is to study the effect of size, the charge of the anions on the crystal structure and on the electrical and magnetic properties of these materials. We have recently characterized two different derivatives of tetrathiafulvalene, **TTF**, and one of *bis*(ethylenedithio)tetrathiafulvalene, **BEDT-TTF**, with the diamagnetic inorganic clusters $[M_6O_{19}]^{2-}$, where M=Mo,W, and we have found that $(TTF)_3[Mo_6O_{19}]$ is a one-dimensional compound, with TTF^{+1} and $TTF^{0.5+}$ arranged as chains of trimers, isolated by the inorganic anions[4]. In search of new organic donor-inorganic acceptor composites, we have studied the chemistry of the above mentioned orga-

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nic donors and the α-Keggin anion $[PMo_{12}O_{40}]^{3-}$ [5], which also exists in the reduced forms $[PMo_{12}O_{40}]^{n-}$, n=4,5 [6]. The molecular structure of the cluster consists of $[PO_4]$ tetrahedron surrounded by four $[Mo_3O_{13}]$ sets, formed by three edge-sharing $[MoO_6]$ octahedra. The $[Mo_3O_{13}]$ sets are linked together through oxygen atoms. There are mainly two reasons why we have chosen this cluster:

a) *the anion can be easily reduced to a paramagnetic mixed-valence cluster* $[PMo_{12}O_{40}]^{4-}$, *without changing its shape ;*

b) *the size of the anion should favour segregated structures.*

In a previous paper we have reported and discussed the magnetic and electrical properties of the TTF derivative, i.e. $(NEt_4)^+(TTF^0)_2(TTF)_4^{3+}[PMo_{12}O_{40}]$ [7]. Here we report and discuss the results of *EPR* and the static magnetic susceptibility of **$(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$** and of **$(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$**, for comparison.

RESULTS

The synthesis and the characterization of $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$ and $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ have been previously reported [8,9].

Structure description

Several attempts have been made to study the crystal structure of $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$; but, due to the low quality of the crystals, we were only able to determine the space group and the unit-cell parameters. The compound crystallizes in the monoclinic space group *I2*: *a*=13.995(4); *b*=43.15(1); *c*=14.068(3)Å; *ß*=107.57(2)°, Z=2, and it appears to be isomorphous to $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$, the structure of which has been already solved [9]. The latter consists of two-dimensional sublattices, made of organic and inorganic layers, alternating along the [010] direction of the monoclinic unit-cell.The BEDT-TTF molecules stack along the direction of the (a,c) plane and they are arranged in two types of stacks: the first one is uniform, while the second one results from a zig-zag mode of stacking of dimers. The shortest S...S intermolecular interactions along the uniform stacks are 3.88 and 4.04 Å and 3.78, 3.84 and 3.89

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Å for the dimerized ones.

Optical spectra

The powder electronic spectra of the compounds have been measured at room temperature and band positions are reported in Table I. The one electron reduced $[PMo_{12}O_{40}]^{4-}$, the green form, shows a very broad absorption band in the visible at about 12,650 cm^{-1}, associated at which is a broad band at 7,200cm^{-1} which have been assigned as intervalence absorptions Mo(V)-->Mo(VI)[10]. The band at 17,500cm^{-1} can be assigned as *d-d* transition of Mo(V) electronic configuration ($^2B_2$ ---->$^2B_1$ in C_4 symmetry). No bands are observed below 5,000cm^{-1} .On the other hand, a very intense and broad absorption at lower energy is observed at 3,800 (0.47eV) in the phosphomolybdate and at 4,000cm^{-1} (0.50eV) in the silicotungstate derivatives. The presence in the near-infrared region of this large broad band, labelled **A** band, is an important feature of *mixed-valence organic charge-transfer* compounds [11]. The infrared spectra of (BEDT-TTF)$_8$[$PMo_{12}O_{40}$] and of (BEDT-TTF)$_8$[$SiW_{12}O_{40}$] were recorded at room temperature and they are similar, except for the fact that absorptions arising from the anion are at different frequencies [12] .

TABLE I . *Diffuse reflectance electronic spectra* [a].

$(NBu_4)_4[PMo_{12}O_{40}]$	31200	17500 sh	12650	8700sh	7200[b]
$(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$	30900	21400	16700	11600	3800[b]
$(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$	30900	21400	16700	11500	4000[b]

[a] *Band positions in* cm^{-1}; [b] *very broad.*

Electrical and Magnetic properties

The single-crystal *d.c.* electrical conductivity at room temperature of (BEDT-TTF)$_8$[$PMo_{12}O_{40}$] has been measured and it has been found to be σ=2x10^{-1}Scm^{-1}. The value is one order of magnitude less than that of (BEDT-TTF)$_8$[$SiW_{12}O_{40}$]. The temperature dependence of *d.c.* electrical conductivity data could be fitted by using the following equation :

$\sigma=\sigma_0\exp[-E_a/k_BT]$ in the temperature range 300K<T<200K and the activation energy, E_a, was found to be ~ 0.1 eV. They are therefore semiconductors. The interpretation of the magnetic properties observed in both compounds is the most interesting aspect of this work. The *EPR* spectra on powdered samples have been recorded at room and at *liq.*N_2 temperatures. The magnetic susceptibility data were acquired by a SQUID magnetometer in the temperature range 2-300K. In unravelling the contributions of the inorganic clusters and the organic donor stacks to the magnetic susceptibility of $(BEDT\text{-}TTF)_8[PMo_{12}O_{40}]$, EPR and static magnetic susceptibility measurements of $(NBu_4)_4[PMo_{12}O_{40}]$ and $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ have been performed. $(NBu_4)_4[PMo_{12}O_{40}]$ is EPR silent at room temperature and it shows a single-line (g=1.9444 , ΔH=50G) with no hyperfine structure at 100K. The molar susceptibility of this compound can be described by the relation: $\chi_M = \chi_{tip} + C/T$, where χ_{tip} is the temperature independent paramagnetism and C is the Curie constant. The best fit was obtained with the following parameters: $\chi_{tip}=7.8\times10^{-4}$ emu/mol and C=0.3402 emuK/mol. The Curie constant and the *g*-value are in agreement with those expected for one unpaired electron per inorganic cluster, localised on one molybdenum atom at lower temperatures. $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ shows a Lorentzian signal, which increases in intensity as the temperature is lowered. The *g*-value is 2.007, and it is constant with the temperature in the temperature range studied. The observed linewidth ΔH is 40 Gauss at 300K. The *g*-value is typical for localised organic radical-ion species[9,13]. The $[SiW_{12}O_{40}]^{4-}$ anion is diamagnetic and therefore the signal is due only to the presence of localised BEDT-TTF spins. The plot of the magnetic susceptibility of $(BEDT\text{-}TTF)_8[SiW_{12}O_{40}]$ *vs* temperature has not been previously reported [9] and therefore it is shown in figure 1. The measured susceptibility was corrected for the diamagnetic contribution of all the atoms. At low temperature the susceptibility shows a Curie-tail and at higher temperatures the value is lower than that expected for a Curie susceptibility: $\chi= N(\mu^2{}_B/k_BT)\rho$, where ρ is the average number of electrons or holes per formula unit. A simple attempt to estimate the Curie tail contribution to the total magnetic susceptibility was accomplished by plotting $1/\chi$ *vs* T in the temperature range 2-20K and the C value was found to be 0.17 emuK/mol. The experimental data

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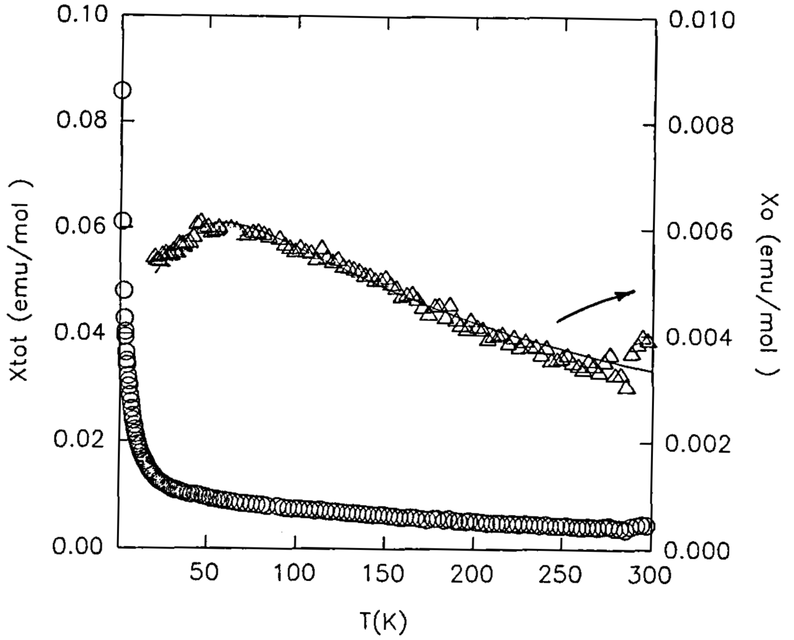

FIGURE 1. Temperature dependence of the total molar magnetic susceptibility (oooo) and of the organic term of the susceptibility (ΔΔΔΔ) of (BEDT-TTF)$_8$[SiW$_{12}$O$_{40}$].

were then corrected by subtracting this contribution, and the resulting plot is reported in figure 1. With decreasing temperature the susceptibility goes through a broad maximum at about T=60K, which is characteristic of short range antiferromagnetic coupling in 1D magnetic systems. The experimental data were fitted with a model for a 1D Heisenberg antiferromagnet on the basis of the crystal structure. Two different types of BEDT-TTF chains are present in the unit-cell. The observed molar susceptibility is then assumed to be the sum of three contributions :

$$\chi_{tot} = 2\,\chi^{1D}_{Heis.} + 2\,\chi_{act} + \alpha/T.$$

The first term represents the temperature dependence of the susceptibility expected for uniform Heisenberg AF chains, the second one the contribution expected for zig-zag dimeric chains (activated magnetic behaviour) and the third one is a paramagnetic contribution due to impurities. The g-value was fixed to the average observed in the *EPR*

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experiments and all the spins ($S=1/2$) were assumed to be localised: *one per dimer*. The data were fitted according to the Bonner-Fisher model[14], adapted by Hall[15] with $J/k_B=-36K$ and the approximate singlet-triplet model with a magnetic gap of $\Delta/k_B= 227K$ and $\alpha=0.172$ emuK/ mol. The J/k_B value is comparable to that found in α'-(BEDT-TTF)$_2$[Ag(CN)$_2$], where a similar 1D uniform dimerised BEDT-TTF magnetic chain structure is present. In the latter the *intra* and *inter* dimeric distances are shorter [13]. The origin of the anomalous paramagnetic contribution is at moment unknown [16]. The temperature dependence of the magnetic susceptibility of (BEDT-TTF)$_8$[PMo$_{12}$O$_{40}$] is reported in figure 2. At low temperature the magnetic susceptibility appears to be Curie-like. At T=300K the value of the susceptibility corrected for core diamagnetism is 8.15×10^{-3} emu/mol. Isothermal magnetization *vs* field at T=6K is linear and the C value corresponds to one unpaired electron. This suggests antiferromagnetic interactions at low temperatures in the organic chain and the presence of one unpaired electron localized on the inorganic cluster. A simple attempt at extracting from the total susceptibility, χ_{tot}, the contribution of the unpaired spins on the BEDT-TTF dimers, χ_0, was accomplished by subtracting both the temperature independent paramagnetism and the Curie susceptibility ($\chi_{tip}+C/T=\chi_{anion}$), estimated for the paramagnetic (NBu$_4$)$_4$[PMo$_{12}$O$_{40}$] :

$$\chi_{tot} = \chi_0 + \chi_{anion}$$

The temperature dependence of organic contribution to the magnetic susceptibility obtained in this way is reported in figure 2. As in the silicotungstate, a broad maximum at about T=70K is observed. This behaviour implies short-range antiferromagnetic interactions along the BEDT-TTF chains. Assuming for simplicity the same crystal structure of the previous compound, the data were fitted according to the Bonner-Fisher model for a chain of antiferromagnetically coupled $S=1/2$ spins (one spin per dimer) and to an approximate singlet-triplet model. The best parameters were found to be $J/k_B=-26K$ and $\Delta/k_B=180K$, respectively.

These results suggest the presence of a similar organic chain structure in both compounds. Further studies are in progress in an attempt to have a complete understanding of the magnetic behaviour, especially in the

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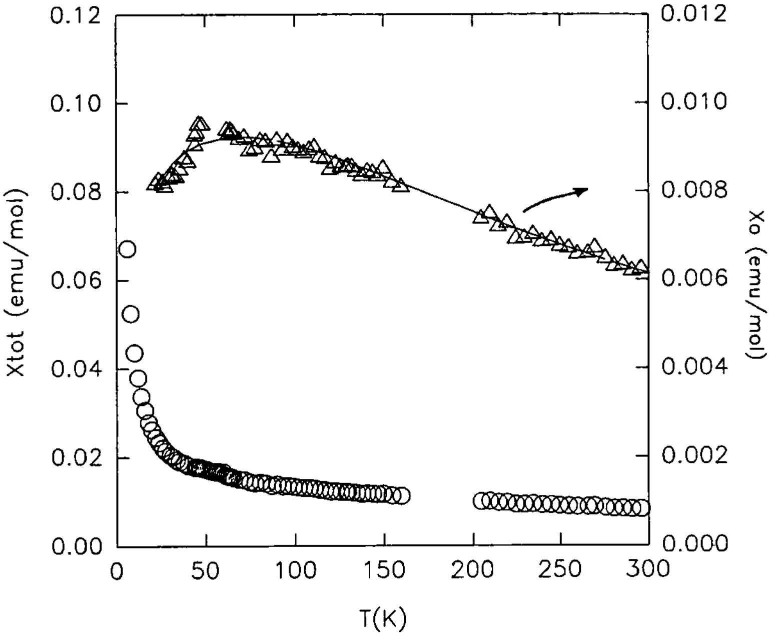

FIGURE 2. Temperature dependence of the molar magnetic susceptibility of (BEDT-TTF)$_8$[PMo$_{12}$O$_{40}$] (oooo) and of the organic contribution of susceptibility (ΔΔΔΔ).

low-temperature region (below 30K) in both compounds.

CONCLUSIONS

The radical-ion salts (BEDT-TTF)$_8$[PMo$_{12}$O$_{40}$] and (BEDT-TTF)$_8$[SiW$_{12}$O$_{40}$] are *Mott-Hubbard* insulators with poor π-electron delocalization between (BEDT-TTF$^{+0.5}$)$_2$ dimers. The magnetic behaviour is typical of a 1D antiferromagnetically exchange-coupled system. In both compounds the dimers are arranged in two different chains: one uniform and the other one distorted.The magnetic and electrical behaviour is likely attributable to an electron localization caused by the combined effect of the presence of strong electron correlations and of the interaction with localized charges and spins on the anions.

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