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PHYSICAL PROPERTIES OF THE DMtTTF SALTS: A NEW SERIES PRESENTING ANTIFERROMAGNETIC GROUND STATES.

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Abstract: The conducting and magnetic properties of three salts of the DMtTTF series are described. Low temperature antiferromagnetic ground states are found for the three compounds. Depending on the anions the crystal organisation is either triclinic (as for the TMTTF salts), or monoclinic. As expected, the position of the magnetic axis is correlated to the crystal symmetry. Finally the origin of the magnetic phase is discussed using the same theoretical framework as for the related TMTTF salts.

INTRODUCTION

Until recently the radical cation salts presenting a low temperature antiferromagnetic ground state were essentially found among the TMTSF\(^{1,2,3}\) (tetramethyltetraselenafulvalene) and TMTTF (tetramethyltetrathiafulvalene) series\(^{4,5,6,7}\). These compounds all present the same raw formula: \((\text{TMTCP})_2X\) (where C = S or Se and where X is a diamagnetic anion) and have the same crystallographic organisation at room temperature\(^8,9\); they are described with the triclinic PI space group. The main features of their crystal structure is the occurrence of sheets of anions separating the organic stacks which are characterized by a "zig-zag" stacking of the TMTCP molecules. As a consequence diads of TMTCP are formed (i.e., two different interchain overlaps should exist) although the TMTCP chains are found to be only weakly dimerised. Moreover, if non-centro-symmetrical, the anions should be statistically disordered to restore the center of symmetry of the structure. If they get ordered at low temperature the pristine unit cell cannot be preserved and the condensation of a superstructure is necessary. Such a phase transition has been experimentally observed for many salts of the series\(^10\). The distinctive properties of the TMTTF salts were recently related to their peculiar molecular organisation which gives rise to comparable positive and negative contributions to the transverse overlap\(^{11}\). To check the validity of this argument the synthesis of new series of compounds presenting closely related crystal structures is clearly useful.

A preliminary study of a new series of radical cation salts based on the DMtTTF (dimethyltrimethylene tetrafulvalene) molecule was recently published\(^{12}\). The elemental analysis revealed the usual 2:1 stoichiometry. The EPR results suggested the occurrence of a low temperature antiferromagnetic ground state for three of these samples, although the moderate quality of the crystals did not allow any more detailed study. In this letter we report the structural and physical properties of three DMtTTF salts of higher quality, two of them were prepared with tetrahedral anions (ClO\(_4\) and ReO\(_4\)), and the last one with an octahedral anion (AsF\(_6\)) and clearly demonstrate the magnetic nature of the low temperature ground state. We finally discuss the correlation existing between the

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observed physical properties and the crystal organisation of these compounds.

EXPERIMENTAL

The synthesis of the DMTTTF molecule was realised as already described. However the last step (i.e. the separation of DMTTTF from TMTTF and HMTTF) was improved: flash chromatography on silica gel with CS\(_2\) as eluant was used. The residual amount of TMTTF or HMTTF after this purification was shown to be less than 0.1\% using a capillary gas chromatograph. The samples were then prepared by the standard electrochemical technique from 1,1,2-trichloroethane.

X-ray intensities were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Cu-K\(\alpha\) radiation. The conductivity measurements were made using a standard four probe technique with platinum paint contacts. The AFMR results were obtained with a standard EPR Varian spectrometer operating at 9.3 GHz (X band).

RESULTS

The crystal structure of (DMTTF)\(_2\)AsF\(_6\) has been already published. A triclinic structure similar to that of the TMTTF salts was found. On the contrary we find (DMTTF)\(_2\)ClO\(_4\) monoclinic (space group C 2/c). The unit cell parameters are:

\[
\begin{align*}
a &= 27.768 \, \text{Å} \\
b &= 7.159 \, \text{Å} \\
c &= 14.040 \, \text{Å} \\
\beta &= 110.86^\circ \\
V &= 2608 \, \text{Å}^3
\end{align*}
\]

A relevant projection of the structure is given in figure 1a. A "zig-zag" stacking of the DMTTF molecules is found along the \(b\) axis. Within the stacks the molecules are related through a screw axis. Since their average plane is perpendicular to \(b\), only one interplanar distance is found (i.e. there is only one intrachain overlap). Noticeable interstack interactions are suggested by the short interchain S-S distances. The main difference between the triclinic (AsF\(_6\)) and the monoclinic (ClO\(_4\)) structures is illustrated in figure 1b which shows that the relative position of the molecules is different in these two cases. Last but not least, it should be noted that the Cl atoms lay on a 2 fold axis in the monoclinic structure (see fig. 1a). Thus no orientational disorder of the ClO\(_4\) can exist. The results concerning the ReO\(_4\) salts are still preliminary. However, the structure of this compound is also monoclinic and similar to that of the ClO\(_4\) salt.

The occurrence of monoclinic symmetries is an important asset obtained with this new series of materials. It is striking that a similar structure has been recently found for the selenium analog (DMTTF)\(_2\)SeO\(_4\). More structural details on the DMTTF salts will be published elsewhere.

The electrical conductivity results are given in figure 2. The room temperature value of \(\sigma\) is about 100, 170 and 250 \(\Omega^{-1}\text{cm}^{-1}\) for the AsF\(_6\), ReO\(_4\) and ClO\(_4\) salts respectively. When decreasing the temperature a metallic behaviour is first observed. Then an electronic localisation is revealed by an exponential increase of \(\sigma\). Due to the formation of "cracks" (usually observed in these series of compounds) the temperature (\(T_{\text{max}}\)) and the amplitude of the maximum of the conductivity cannot be precisely determined. The results given in figure 2 include a dashed line which represents an extrapolation between the high and low \(T\) behaviour. Nevertheless the comparison with the corresponding TMTTF salts (as an example the conductivity of the AsF\(_6\) salt is also given in figure 2) leads to the conclusion that the metallic behaviour of the DMTTF salts is more pronounced: a higher value of \(\sigma_{300K}\). a lower estimation of \(T_{\text{max}}\) are found. Moreover a lower value of the gap in the localised regime \(\Delta = 200 - 300K\) (instead of 600 - 800K for the corresponding TMTTF salts\(^{13}\)) is also measured. Note that, despite the occurrence of cracks,
EPR results concerning samples containing a residual amount of TMTTF were already published. As expected, the occurrence of a few percent of impurities does not drastically change the magnetic behaviour and similar results were obtained with the new batch. The EPR linewidth is first a decreasing function of $T$ down to 20-30K and then increases quickly at lower temperature. At the same time the paramagnetic susceptibility remains high and weakly temperature dependent. This behaviour suggests the occurrence of growing antiferromagnetic (AF) fluctuations as $T$ is reduced below 20K. One way to prove the condensation of an AF ground state is to detect an antiferromagnetic resonance (AFMR). This technique was already successfully applied using a conventional X band spectrometer to the study of the magnetic ground state of several TMTTF salts. With this method, characteristic rotation patterns are obtained which give the resonance field (usually far from $\omega / \gamma = 3300$ Gauss) as a function of the rotation angle. When the temperature of the experiment is low compared to the transition temperature ($T_n$) the fit of the results requires two parameters $\Theta_0$ and $\Theta_4$ which are the zero field uniform spin wave frequencies. In this low $T$ limit, $\Theta_0 / \gamma$ (where $\gamma$ is electron gyromagnetic ratio) is also the spin-flop field. Moreover the comparison between the experimental data and the theory gives an estimate of the position of the magnetic axes.

We found the AFMR for the three studied compounds. The Neel temperature $T_n$ is about 9 K for the AsF$_6$ and ClO$_4$ salts. The long range magnetic order is only observed below $T_n = 3.5$ K for the ReO$_4$ salt. Rotation patterns obtained at 2.5K for the AsF$_6$ and the ClO$_4$ are given in figures 3 and 4. The rotation axes are either the stacking axis or the direction of the maximum of the g factor (long axis of the organic molecule). Typical fits obtained using the standard AFMR theory are also given.

FIGURE 2: Electrical conductivity of the DMTTF salts. Note that the low temperature activation energy is smaller than for (TMTTF)$_2$AsF$_6$ also given for comparison.
For the AsF₆ salt a “bubble” is found when rotating the crystal around a. This pattern characterises the situation where q₂ is slightly above the applied microwave frequency. The rotation around q₃ max indicates a misorientation of the magnetic axes relative to the crystallographic frame since the minimum of the resonance field is not found in the direction perpendicular to q. A similar result was already obtained for the TMTTF salts presenting an AF ground state and is the expected consequence of the triclinic symmetry. The misorientation also affects the shape of the bubble which becomes slightly unsymmetrical. Finally the fits give q₂ and q₃ and an estimate of the position of the magnetic axes. The easy, intermediate and hard axes are respectively close to b = a x c*, c and a, in directions close to that already found for (TMTTF)₂SCN and (TMTTF)₂SDF₆. The angle between the hard axis and a is about 13°. The projection of the easy axis in the (b’, c’*) plane is situated approximatively along the direction of q₃ (short axis of the DMTTTF molecules). Moreover we find q₃/y = 3.35 K Gauss and q₁/y = 5.2 K Gauss.

The rotation patterns obtained for the ClO₄ salt are characteristic of the case q₂ < q₁ < q₃. For this salt, no misorientation is observed since the resonance field is extremum at 90° from the stacking axis b which is exactly the hard axis. This is in agreement with the monoclinic crystal symmetry which implies that b is a principal magnetic direction. The easy and intermediate axes are at about 10° from the direction of q₃ (short axis of the DMTTTF molecules). The best fits are found for q₁/y = 2.3 K Gauss and q₃/y = 3.5 K Gauss.

For the ReO₄ salt we got quasi-sinusoidal rotation patterns as expected when the experimental temperature (2.5 K) is only slightly below Tₙ. The position of the magnetic axes is close to that already found for the ClO₄ salt and q₂/y = 0.9 K Gauss, q₁/y = 1.3 K Gauss. The determination of the spin-flop field now requires the extrapolation at T = 0 of q₁(T) which gives the rough estimate q₁(0) = 1.5 - 2. K Gauss.

**CONCLUDING REMARKS**

The first noticeable result concerning the DMTTF and DMTTTF series is the conducting behaviour. Although the DMTTF molecule is non-symmetrical, high conductivity can be obtained (σ is better for a DMTTF anion than for the corresponding TMTTF salt). As expected, non-symmetrical molecules are easily incorporated to realise a zig-zag stacking of the conducting chains. Contrary to the TMTTF series, both triclinic and monoclinic samples are found with the DMTTF molecule. It is noteworthy that monoclinic symmetry is found with the tetrahedral anions. Realising that these anions are disordered in the triclinic (T) phase and ordered in the monoclinic (M) structure, it may be argued that the latter crystal organisation allows the anion ordering without the lack of elastic energy required by the condensation of a superstructure.

As far as the organic lattice is concerned, figure 2b shows that the N and T crystal structures present some similarities. In particular both structures imply the existence of negative and positive contributions to the transverse overlap as already found in the TMCF series and it may be argued that this singular situation favors the AF ground state. An alternative explanation for the occurrence of antiferromagnetism may be the weaker localisation found in the DMTTF series (compared with that observed for the corresponding TMTTF salts). Such an explanation has already been used to discuss the competition between electronic instabilities in the TMTTF series.

With the exception of the position of the magnetic axes which directly results from the crystal symmetry, the parameters of the AF ground state (T and q₂) and the monoclinic ClO₄ salts. The obtained values are close to that already found for the TMTTF salts. Smaller values of q₂ are found for the ReO₄ but this is the consequence of a smaller Tₙ and the ratio q₂/q₁ remains almost the same for all the compounds.

In summary the physical properties of the DMTTF and DMTTTF salts are closely related. With this new series, we have shown that the possibility of finding antiferromagnetism is not restricted to the TMCF series (C = S or Se) but can be extended to new compounds grown with unsymmetrical molecules. Moreover the triclinic structure of the TMTTF salts is not a necessary condition to observe the AF state either. However, some characteristics of the local structural organisation of these compounds may be relevant to determine the topology of their low temperature phase diagrams.

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