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Electronic magnetic resonance in a series of antiferromagnetic molecular perovskites

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Abstract. — The magnetic properties of a series of ternary tetrathiafulvalenium (TTF\(^+\)) salts incorporating, within a unique antiperovskite structure, a discrete halide \((Y = Cl, Br\) or \(I\)) in addition to an octahedral molybdenum halide cluster dianion \(Mo_6X_{14}^{2-}\) (with \(X = Cl\) or \(Br\)), are described. The preparation and structural chemistry of the materials of general formula \(((TTF^+)_3(Mo_6X_{14}^{2-})_2(Y^-)\) are briefly recalled. The single-crystal electronic magnetic resonance is explored in details using an X-band ESR spectrometer, both in the paramagnetic state where a narrow EPR signal is observed, as well as in the low temperature antiferromagnetic phase where antiferromagnetic resonance (AFMR) is detected. A quantitative discussion of the resonance field and linewidth is given in both regimes. The EPR line characteristics are shown to be strongly sensitive to the TTF\(^+\) environment, namely, the nature of the halide on both anion sites and small variations in intermolecular interactions, which reveal the importance of the spin-orbit coupling. On the other hand, AFMR data are discussed in terms of a dominant dipole-dipole interaction as found previously for other TTF-based cation radicals salts. Finally, similar albeit contrasted results are obtained with the isomorphous, chalcohalide rhenum cluster dianion-based ternary salt \(((TTF^+)_3(Re_6S_6Cl_{12}^-)(Cl^-)\), which allow for a discussion of the AFMR lineshape.

Introduction.

This paper reports a comprehensive investigation by X band spectroscopy of the magnetic interactions between molecular ions aggregated within a precise, supramolecular organization. Indeed, in these series of ternary tetrathiafulvalenium (TTF\(^+\)) salts of general formula \(((TTF^+)_3(X^-)(Y^-)\), where \(X^- = Mo_9Cl_{14}^-\), \(Y^- = Cl^-\), \(I^-\) (abridged notation : Cl/Cl) ; \(X^- = Mo_9Br_{14}^-\), \(Y^- = Cl^-\), \(Br^-\), \(I^-\) (Br/Br) ; \(I^-\) (Br/I) and \(X^- = Re_9S_6Cl_{12}^-\), \(Y^- = Cl^-\), \(Br^-\), \(I^-\) (Br/I) and \(X^- \times Y^- = 5\), organic cation radicals with unpaired electron spins \((S = 1/2)\) have been induced to fit within the desired, rhombohedrally distorted perovskite structure [1]. As a manifestation of the long-range symmetry of the materials, all five compounds present a typical

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rhombohedral shape of the single-crystals [1], which proved to greatly facilitate the electronic magnetic resonance experiments. Since the molecular inorganic cluster dianions are diamagnetic, the paramagnetic behaviour originates from the presence of the TTF$^+$ spins only. Thus, narrow ESR signals are observed whose linewidth is of the same order of magnitude as that of other TTF-based organic cation radical salts [2]. However, a salient, distinctive characteristic of the present series is to be found in the observation of different variations of the EPR linewidth for different halides, on both anion sites. In addition, the EPR linewidth was eventually found to be very sensitive in some preparations to even minute amounts of substitutional I/Cl disorder on the discrete halide site Y. Moreover, the g-factor changes along the series, a consequence of small structural modifications of the TTF molecular geometry.

At low temperatures, an antiferromagnetic ordering is observed with Néel temperatures of the order of 10 K. Since the AFMR signal also originates from the spins of the TTF molecules, it can be studied with the same X band spectrometer. The high rhombohedral (R$3\overline{3}$) symmetry of the system allows for an unprecedented, detailed analysis of the rotation patterns of the resonance. The antiferromagnetic parameters evolution in the series is much less sensitive to the nature of the halide and can be correlated with the evolution of $T_N$. This suggests that the relevant energy for the magnetic anisotropy is the dipole-dipole interaction. This argument is further supported by the estimation of the magnitude of this interaction. In addition, a structured AFMR line is observed in the molybdenum halide cluster series whereas a single line is found in the isomorphous salt of a chalcophile rhenium cluster, (TTF$^+$)$_3$(Re$_6$S$_6$Cl$_3$$^-$$(Cl^-)$ [1c, d]. We believe that this remarkable difference is a manifestation of different magnetic superstructures between the two types of salts.

Electrochemical crystal growth. The particular cases of some of the Cl/Cl batches and the Br/I samples.

These molecular perovskites are grown as high purity single-crystals by constant low current oxidation at a platinum wire anode of the neutral TTF molecules in the presence of alkylammonium (R$_4$N$^+$) salts of Mo$_6$X$_{12}$$^-$ and the corresponding halide Y$^-$, in a common organic solvent [1a, b, c]. It is of interest to note that some of the Cl/Cl batches prepared during the early stages of this research were in fact obtained in the presence of R$_2$N$^+$I$^-$ in the electrochemical cells. It was in fact discovered that the phase (TTF)$_3$(Mo$_6$Cl$_{14}$) (Cl), 1, was obtained this way rather than the expected phase formulated (TTF)$_3$(Mo$_6$Cl$_{14}$)(I). We designed a specific synthesis of 1 using tetrphenylammonium chloride as a source of chloride, hence the obtention of single-crystals of 1, of an improved purity and labelled Cl/Cl, bath C in the following. Similarly, single-crystals of 4 (Br/I) are necessarily obtained using R$_4$N$^+$I$^-$ and, therefore, minute amounts of Br to I substitutional disorder at some of the outer halide sites of the molybdenum bromine clusters cannot be ruled out. This accounts for the observed dispersion of the EPR data for some of these samples.

Structural chemistry.

All five compounds are isostructural, space group R$3\overline{3}$. In the spirit of a classical description of the perovskite structure [3], 1-5 can be thought of as being built up by the stacking of pseudo-close-packed (TTF$^+$)$_3$(X$^-$)$^2$ layers which form octahedral holes occupied by the discrete halide ions Y$^-$ [1a, b]. Three such layers, labelled A, B and C in Figure 1a, are required in the unit-cell. Because of the rhombohedral distortion, there is only one stacking direction in the structure, that is, the layers of organic spins are stacked along the unique threefold inversion axis, as shown in figure 1b. Note that the discrete halide sites, a distinctive feature of this structure, are located at the center of corner-sharing, centrosymmetrical pseudo-
Fig. 1. — a) Construction of the structure of the molecular perovskites (TTF)$_2$(Mo$_6$X$_{14}$)(Y) by the superposition of three layers such as A, B and C along the single 3 axis. b) A projection of the structure along a direction orthogonal to 3.

\{(TTF$^+$)$_6$Y$^-$\} octahedral units [1]. Except for 1 and 5, a small but significant distortion of the molecular skeleton is found [1b]. This distortion is both cluster and discrete halide dependent in the molybdenum series and is such that the molecular D$_{2h}$ symmetry is not preserved while maintaining the centrosymmetry.

**Resonance in the paramagnetic phase.**

The EPR experiment were made with a Varian X-band spectrometer operating at 9.3 GHz and equipped with an Oxford ESR 900 helium cryostat.

Narrow EPR lines are observed for all compounds. We first describe the results for (TTF$^+$)$_3$(Mo$_6$Cl$_{28}$$^+$)(Cl$^-$), then compare with the other members of the series. Finally a discussion of the results is given.

1. (TTF$^+$)$_2$(Mo$_6$Cl$_{24}$$^+$)(Cl$^-$). — As expected from the crystal structure, a uniaxial symmetry is found with a degeneracy in a plane perpendicular to the three-fold axis and extrema of the $g$ factor and linewidth are found along and perpendicular to this axis.
Let us first consider the influence of the sample preparation on these extremum values. As already mentioned, we have prepared different sample batches. Even for high quality crystals carefully checked by X-rays, a dispersion of the EPR parameters was observed, as shown in table I, although reproducible results were found inside any single batch. The fact that large variations of the linewidth are observed is particularly striking. Likewise, smaller variations of the \( g \) factor are correlated with these variations. Note that the batch C for which the smallest \( g \) and linewidth are found corresponds to the preparation without possible inclusion of iodine.

Table I. — EPR parameters (\( g \) and linewidth) among the series. The indices // and \( \perp \) stand respectively for parallel and perpendicular to the \( \overline{3} \) axis. \( g_\perp \) and \( g_\parallel \) are the deduced molecular \( g \) values.

<table>
<thead>
<tr>
<th>Mo series</th>
<th>( g_\parallel )</th>
<th>( g_\perp )</th>
<th>( \Delta H_{\parallel} \text{(gauss)} )</th>
<th>( \Delta H_{\perp} \text{(gauss)} )</th>
<th>( g_\gamma )</th>
<th>( g_\chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl/Cl batch A</td>
<td>2.0044</td>
<td>2.0107</td>
<td>13.7</td>
<td>19.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl/Cl batch B</td>
<td>2.0041</td>
<td>2.0105</td>
<td>7.7</td>
<td>12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl/Cl batch C</td>
<td>2.0038</td>
<td>2.0099</td>
<td>3.1</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/Cl</td>
<td>2.0057</td>
<td>2.0116</td>
<td>8.2</td>
<td>8.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/Br</td>
<td>2.0058</td>
<td>2.0121</td>
<td>10.1</td>
<td>11.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/I</td>
<td>2.0056</td>
<td>2.0125</td>
<td>44</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl/Cl (Re)</td>
<td>2.0040</td>
<td>2.0096</td>
<td>18</td>
<td>22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In figure 2 we give the room temperature rotation patterns, i.e. the \( g \) factor and linewidth as a function of the magnetic field orientation for samples of the batch C. Because of the symmetry, this figure is representative of any rotation plane containing the three-fold axis. The rotation patterns of both the \( g \) factor and linewidth can be fitted to a \( \cos^2 \theta \) like dependence. A similar variation is found for samples from other batches. These fits are given by the continuous lines in figure 2.

Figure 3 shows the temperature dependence of the linewidth, with the magnetic field along the \( \overline{3} \) axis, for samples of the three different batches. Samples of batch C present a quasi-linear temperature dependence of the linewidth. On the contrary, the other samples show a minimum followed by an increase of the linewidth at lower temperatures, the amplitude of which being correlated with the room temperature absolute value. These results suggest that the observed enhancement of the linewidth has an extrinsic origin which will be discussed in more details in the following and we now proceed with a more detailed discussion of samples of batch C.

Figure 4 illustrates in more details the temperature dependence of the EPR behaviour of these samples. Figure 4a shows that the linewidth decreases almost linearly with \( T \) for both field directions in the paramagnetic phase. In addition, the \( g \) factor (Fig. 4b) is almost temperature independent.

At low temperatures, small precursor effects are observed before the EPR signal abruptly disappears within less than one degree. This is the signature of the onset of the antiferromagnetic ordering identified earlier by static magnetic susceptibility measurements [1a]. The Néel
temperature is estimated to be $T_N \sim 9$ K. For samples of batches A and B showing a significant enhancement of the EPR linewidth at low temperatures, the transition appears more gradually. This confirms the existence in those samples of a weak extrinsic component of the signal which eventually remains paramagnetic at lower temperatures.

Note, finally, that the deduced spin susceptibility reproduces with less accuracy the results already obtained from squid measurements [1a], with in particular a high temperature Curie-Weiss dependence ($\theta_{CW} \approx 14$ K).

2. Other samples of the molybdenum series. — We now compare the results obtained with the other members of the series (compounds 2, 3, 4).

The room temperature parameters of the EPR signal among the series are given in table I.
They are similar to those previously described for the Cl/Cl salt. Dispersion between different batches were particularly found for the Br/I salt for which strictly nominal purity is impossible to achieve, as discussed previously. As for the Cl/Cl salt (see Figs. 3 and 4), the linewidth difference between batches can be larger than the anisotropy for a given batch. In the same way, small differences are found in the $g$ values. The results for the samples with the smallest low temperature plateau are given in table I.

The remaining part of the discussion focuses on the comparison of the Cl/Cl, Br/Cl and Br/Br crystals. Figure 5 gives the temperature dependence of the linewidth with the magnetic field along the $\overline{3}$ axis. As for the Cl/Cl salt, a linear dependence is found for Br/Cl down to low temperatures. On the other hand a small plateau is still observed for the Br/Br compound. All three compounds have essentially temperature independent $g$ factors. The room temperature values are given in table II. Note that the $g_f$ value is identical (within the experimental accuracy) for the bromide cluster compounds and is larger than that observed for the Cl/Cl salt. In the plane perpendicular to the three-fold axis, one observes a continuous evolution in the series. In the same way, the linewidth increases with the size of the cluster and that of the halogen as well.

As mentioned previously for the Cl/Cl salt, the measured spin susceptibility is in agreement with static measurements. All the samples experience an antiferromagnetic ordering, as revealed by the disappearance of the EPR signal. Table II gives the corresponding Néel temperature $T_N$ together with the Curie-Weiss temperature $\theta_{\text{CW}}$ deduced from the magnetic susceptibility in the paramagnetic phase. The fact that $\theta_{\text{CW}}$ is systematically larger than $T_N$ should be related to some anisotropy of the magnetic interactions.

3. (TTF$^+$)$_3$(Re$_8$S$_8$Cl$^{2-}_6$(Cl$^-$)). — This compound, isomorphous to the molybdenum halide cluster series proved to be useful for a comparative discussion of the antiferromagnetic resonance. We describe its EPR behaviour briefly. The room temperature parameters are reported in table I.

The $g$ factor is almost independent of temperature and approximately equal to that for the Cl/Cl crystals of the molybdenum series, showing a close similarity between the two salts. On the other hand, the linewidth (Fig. 5) is much larger and a broad plateau is found below 80 K.
Fig. 4. — Temperature dependences of a) the linewidth and b) $g$-factor for compounds Cl/Cl, batch C with the field along (black symbols) and normal to (open symbols) the $\overline{3}$ axis.

4. Discussion of the ESR results. — After a brief analysis of the influence of the preparation, we concentrate the discussion on the results obtained reproducitively, i.e. the $g$ factor values and the linear dependence with temperature of the linewidth.

a) $g$ factor: Since the $g$ factor is independent of temperature (with the exception of small precursor effects), we essentially discuss the room temperature values given in table I. The results can be summarized as follows:

- A uniaxial symmetry of the $g$ tensor is found. Because the structure contains three
Fig. 5. — Temperature dependence of the linewidths for the following compounds: Cl/Cl (black circle), Br/Cl (black squares), Br/Br (black triangles) and (TTF)$_2$(Re$_8$S$_6$Cl$_6$)Cl. 5 (open circles), with the field along the $\overline{3}$ axis.

Table II. — Magnetic parameters among the series. $\theta_{CW}$ and $T_N$ are respectively the Curie-Weiss and the Néel temperatures. $H_0'$ and $H_+'$ are the effective parameters defined in the text. $H_-$ and $H_+$ are the deduced anisotropy fields.

<table>
<thead>
<tr>
<th>Mo series</th>
<th>$\theta_{CW}$(K)</th>
<th>$T_N$(K)</th>
<th>$H_0'$(kG)</th>
<th>$H_+'$(kG)</th>
<th>$H_0$(kG)</th>
<th>$H_+$(kG)</th>
<th>$H_-$(kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl/Cl</td>
<td>14</td>
<td>8.5</td>
<td>3.39 (3.50)</td>
<td>5.35</td>
<td>5.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.23 (3.21)</td>
<td>5.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/Cl</td>
<td>17</td>
<td>9</td>
<td>3.49</td>
<td>5.31</td>
<td>5.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.31</td>
<td>5.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/Br</td>
<td>12</td>
<td>7.5</td>
<td>3.33</td>
<td>3.67</td>
<td>3.7</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.25</td>
<td>3.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br/I</td>
<td>12</td>
<td>5.5</td>
<td>3.55</td>
<td>2.12</td>
<td>2.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.25</td>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl/Cl</td>
<td>12</td>
<td>5.5</td>
<td>3.34</td>
<td>2.03</td>
<td>2.03</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

- symmetry-related TTF orientations, the observed signal is the average between the three corresponding $g$ tensors, each of them having the symmetry of the TTF molecule.

- The $g$ values differ in the series of salts although their structures, particularly the orientation of the TTF molecules, remain very similar. This implies that the individual molecular $g$ tensor is changing.
The $g$ tensor has been measured in many radical cation salts. Quite generally, three different eigenvalues are found, labeled $g_z$, $g_y$ and $g_x$ with eigendirections respectively along the normal, short and long molecular axes of the molecule. Typical values for (TTF+$^+$) are $g_z = 2.0020 \ (5)$, $g_y = 2.008 \ (1)$ and $g_x = 2.014 \ (1) \ [2]$. These values are understood in the frame of the general theory for ion radicals [4], considering the spin-orbit coupling as a perturbation. In particular, $g_z$ is very close to the free electron value because of the symmetry of the highest occupied molecular orbital (HOMO). The same analysis shows that the other two components are not only determined by the nature of the HOMO but also depend on the energy and symmetry of the occupied and unoccupied molecular orbitals. In particular, the symmetry of bonding orbitals plays an important role and substitutions on the TTF core can change the $g$ values in a subtle way. Modifications of the molecular environment are also relevant. Note for comparison purposes that the $g$ values for TMTTF+$^+$ in the Bechgaard salts are $g_z = 2.0021$, $g_y = 2.0090$ and $g_x = 2.0110 \ [5]$. Also note that the largest perturbation occurs for $g_z$. Likewise, exceptionally large $g_x$ values were found in some TTF-based cation radical salts, the other two components keeping standard values [6].

In the present case, the experiment provides two independent $g$ values only, which are function of the eigenvalues of the molecular $g$-tensor. Thus, one value is missing and an additional hypothesis is necessary. We shall thus assume that $g_z$ is equal to 2.0020 since the symmetry of the HOMO is likely to be preserved. Then, the $g$ values along the short and long molecular axes are deduced for the molecular orientations within the structure, as schematized in figure 6. The relevant relations are:

$$
g_{\parallel} = g_z \sin^2 \theta + g_y \cos^2 \theta
$$

$$
g_{\perp} = \frac{1}{2} \left( g_z + g_y \cos^2 \theta + g_x \sin^2 \theta \right)
$$

where $\theta$ and $x$, $y$ and $z$ are the molecular axes defined in figure 6 ($g_z = 2.0020$). For all compounds, $\theta$ is close to 38°.

Fig. 6. — a) Orientation of the molecular $g$-tensor and b) orientation of the molecular plane within the selected orthogonal reference crystal system (Z is the $\bar{3}$ axis).

The results are given in table I. Since $g_z$ only depends on $g_{\parallel}$ and $g_{\perp}$, $g_x$ is almost the same for the two Cl/Cl compounds (1 and 5) and for all Br/Y salts (2, 3 and 4) but differs between the two groups. On the other hand, $g_y$ changes continuously in the series.

A detailed discussion of these results would require a theoretical calculation of the $g$ factor and is left for a future publication. However, several remarks can be made. First, exceptionally large $g_y$ values are associated with those salts in which the TTF molecules is distorted, that is,
for the Mo₆Br₁₄ salts only. However, the distortion is not the same among Mo₆Br₁₄ salts [1b] although \( g_z \) remains the same. This suggests that the TTF distortion is not the only relevant parameter, the nature of the cluster being probably important. On the other hand, the discrete halide is also effective at imposing the \( g_z \) value. In any case, our results show an extreme sensitivity of the \( g \) factor to the TTF environment.

b) Linewidth: Since we consider that the observed plateau is essentially extrinsic, we shall concentrate the discussion on the comparison of salts for which a linear dependence of the linewidth is found in a large temperature domain, i.e., the Cl/Cl (batch C), Br/Cl and Br/Br salts of the molybdenum series.

As reported in table I, a weak anisotropy of the linewidth is found with a maximum in the plane perpendicular to the \( \bar{3} \) axis. Moreover, the linewidth increases from Cl/Cl (batch C) to Br/Cl and Br/Br. This again suggests an effect of the TTF environment, with an increase of the linewidth with the spin-orbit coupling of the two types of halogen, i.e., discrete or bound to the cluster core.

To discuss the temperature variations independently of the absolute value we now compare normalized data. One possibility is to extrapolate the linear dependence down to 0 K to deduce a zero-temperature linewidth dependent on both the sample and field direction. Then, we plot the linewidth normalized by this new parameter. Results are given in figure 7. As far as the linear behaviour is concerned, a single straight line is found for all the Mo₆Br₁₄ salts. In the same way the Cl/Cl salt I gives another straight line with a smaller slope. Figure 7 also shows that the deduced line is independent of the field direction. In conclusion, this means that the linewidth reads:

\[
\Delta H = \Delta H_0 \left( 1 + \frac{T}{T_0} \right)
\]

where the linewidth \( \Delta H_0 \) depends both on the sample and the field direction. \( T_0 \) is a characteristic temperature which depends solely upon the nature of the halogen on the cluster. For the Mo₆Br₁₄ salts one obtains \( T_0 = 115 \text{ K} \) to be compared to \( T_0 = 200 \text{ K} \) for the chloride cluster, Mo₆Cl₁₄.

![Graph](image)

Fig. 7. — Temperature dependence of the normalized EPR linewidths (see text) for the following compounds: Br/Br (black squares), Br/Cl (open circles), Br/I (open squares), with the field parallel to the \( \bar{3} \) axis, superimposed to those for Cl/Cl (black and open triangles) at the two different field orientations.
The physical origin of \( T_0 \) should be found in the relaxation mechanism responsible for the increase of the linewidth with temperature. A simple possibility lies in the spin-phonon coupling. In this case, the characteristic temperature \( T_0 \) is proportional to the Debye temperature which characterizes the lattice excitations. Thus, our results indicate that the spectrum of the acoustic phonons is essentially determined by the cluster, the lattices with the Br clusters being solfter than those incorporating Cl clusters. This may be regarded as a straightforward physical manifestation of the larger polarisability of bromine when compared to that of chlorine.

Antiferromagnetic resonance.

We now proceed with the description of the AFMR results. They were obtained with the spectrometer already used for EPR as for many other TTF-based radical cation salts [7]. As for the EPR, we first describe the results for the Cl/Cl salt of the molybdenum series.

1. (TTF\(^+\))\(_2\)(MoO\(_2\)Cl\(_4\)\(^-\))(Cl\(^-\)). — Below the Néel temperature, an antiferromagnetic resonance is observed, as revealed by a complex signal composed of several single lines. Reproducible results were obtained among different preparations, supporting earlier suggestions that the anisotropy in the antiferromagnetic state is not dominated by spin-orbit coupling in TTF based compounds, but rather by dipolar interactions [8]. Indeed, it is shown in the following that such interactions allow for a quantitative explanation of the AFMR results.

The AFMR experiments consist in determining the parameters of the resonance out of a series of rotation patterns. The present data were obtained with oriented single crystals, allowing rotations of the static magnetic field in simple planes, either containing or perpendicular to the \( \tilde{3} \) axis. The data were taken at a fixed temperature, \( T_{\text{exp}} = 4.5 \text{ K} \).

Figure 8 gives examples of the recorded AFMR signal. In figure 8a and b, the magnetic field is in the plane perpendicular to the \( \tilde{3} \) axis. The spectrum given in figure 8a is taken by scanning the field with a standard velocity (500 G/mm). It gives the gross characteristic of the spectrum. Three strong components can be distinguished. Each component is in fact structured, as seen more clearly in figure 8b. The latter is obtained for another position of the magnetic field in the same plane and with a lower scan velocity (125 G/mm) as well. For the latter orientation, only two components are separated. Note that each of them appears to be composed of several lines. Finally, figure 8c shows the evolution of this spectrum after a rotation of the magnetic field of 35° in the direction of the \( \tilde{3} \) axis. The signal has been shifted at higher field. The three components are now separated and two of them are at least composed of three lines.

Figure 9a shows the evolution of the resonance field of the three main lines of figure 8a, rotating the magnetic field in the plane perpendicular to the \( \tilde{3} \) axis. Cosine profiles are suggested. In fact, the continuous lines correspond to fits with \( H_\Gamma = H_0 + h \cos 2(\theta - \theta_0) \). For the three lines, a very similar value is obtained, \( H_0 = 3.34 \text{ kG} \), corresponding to the resonance field of the EPR line. The values of \( h \) range from 110 to 150 G. The values of \( \theta_0 \) are respectively \(-70°\), \(-10°\) and \(60°\), i.e., separated by approximately \(60°\) (note that the origin of the angles is arbitrary). This 3 fold symmetry which also appears in figure 8c is clearly reminiscent of the crystal symmetry.

Figure 9b gives the resonance field of each main component of the resonance as a function of the angle between the field direction and the \( \tilde{3} \) axis, starting from an orientation where only two components are distinguished (as in Fig. 8b). This shows that the components of the composite signal follow very similar rotation patterns. In particular, they all experience a divergent resonance field when approaching the \( \tilde{3} \) axis. Finally, for a field position where one of the three major components is well separated, its linewidth was followed for a rotation similar to that
Fig. 8. — AFMR signals for Cl/Cl for several field orientations, as follows: a) with the field normal to the 3 axis; b) a novel field orientation, again normal to the 3 axis, albeit at lower scan velocity (see text) and c) for a field orientation at 55° of the 3 axis.
Fig. 9. — a) Resonance field for the three main components of the AFMR signal for Cl/Cl, rotating the field in the plane normal to the $\bar{3}$ axis. b) Resonance field for a rotation into a plane containing the $\bar{3}$ axis. c) Linewidth of a single component for a rotation similar to b). In all three cases the solid lines are fit of the data to the analytical expressions of the AFMR theory, as discussed in the text.

described in figure 9b. As shown in figure 9c the linewidth also presents a divergence. Note that the solid lines in figure 9 represent the fits of the data to the AFMR theory.

2. Other salts of the molybdenum series. — Similar results were obtained with the other molybdenum salts. With the bromine cluster $\text{Mo}_6\text{Br}_{14}$ (2, 3 and 4), it is even more difficult to separate the different components of the AFMR signals. Thus, we have essentially studied the
resonance field rotation patterns. Figure 10 gives the rotation patterns for the Br/Cl and Br/Br salts for orientations comparable to that of figure 9b. Their topology is similar. For the Br/I salt a quasi-sinusoidal rotation pattern with extrema around 2.5 and 3.5 kG is found but a separation of the different components is impossible. We discuss this new topology and the parameters deduced from these results in the following section.

3. (TTF')₃(Re₆S₆Cl₂⁻)(Cl⁻). — In contrast with the samples of the molybdenum series a single AFMR line is observed for this salt. Within the experimental accuracy (including the accuracy on the sample orientation), the resonance field ($H_r \sim 3300$ G) and the linewidth

Fig. 10. — Rotation patterns similar to those in figure 9b for a) Br/Cl and b) Br/Br.
(26 G) are constant in the plane perpendicular to the 3 axis (i.e. the degeneracy is the same as in the paramagnetic phase). In terms of $g$ factor, the result is very close to the paramagnetic value (the corresponding $g$ factor is $g_{\text{AF}} = 2.013$ to be compared with $g_{\text{epr}} = 2.0099$). A rotation in a plane containing the 3 axis gives the results summarized in figure 11. Quasi-sinusoidal patterns are found for both the resonance field and the linewidth. The fit (continuous lines) will be discussed in the next section.

Fig. 11. — AFMR rotation patterns for a) the resonance field and b) the linewidth for a rotation in a plane containing the 3 axis for (TTF)$_3$(Re$_8$S$_6$Cl$_8$)(Cl).
4. Discussion of AFMR results. — The most striking result is the difference between the rhenium and molybdenum salts. We first proceed with the discussion for $(TTF^+)_3(Re_6S_6Cl_8^2-)\) for which the simpler results are found.

a) $(TTF^+)_3(Re_6S_6Cl_8^2-)\): Let us first discuss the orientation dependence of the resonance field. The observed degeneracy implies that the structural symmetry is preserved in the antiferromagnetic phase. Since the resonance field has the EPR value in the degenerate plane, we immediately conclude to the presence of an easy plane (the hard direction being along the $\bar{3}$ axis) with two magnetic sublattices. Therefore, we now give a brief summary of the AFMR in this special case.

The theory of AFMR requires first the determination of the spin orientation for a given strength and orientation of the magnetic field. The second step consists in the determination of the frequency of collective excitations of the spins around the equilibrium (two modes are found as a consequence of two magnetic sublattices) \[9, 7b\]. The case of interest is probably the simpler since the spin orientation is easily determined regardless of the magnetic field orientation. Introducing as usual:

\[ M = M_A + M_B, \quad M' = M_A - M_B \]

it is straightforward to show that $M'$ is in the easy plane and perpendicular to the magnetic field. The second step is therefore analytic and one finds the frequency of the two modes (labelled with $+$ or $-$) as:

\[ \frac{\omega^2}{\gamma^2} = \frac{H^2 + H_+^2}{2} \pm \frac{\sqrt{(H^2 - H_+^2)^2 + 4H^2H_+^2\cos^2\phi}}{2} \]

where $\gamma$ is the gyromagnetic factor, $H_+ = \Omega_+ / \gamma$ is the field which is related to the anisotropy in the hard direction. $H$ is the magnetic field strength, $\phi$ the angle between this field and the hard axis. Figure 12 gives the plot of these frequencies as a function of $H$ for different field orientations. Working at fixed frequency, one eventually cuts one of the two branches to obtain
Fig. 12. — Normalized plots of the antiferromagnetic resonance frequency as a function of the magnetic field in the uniaxial case (easy plane plus hard axis) with a) the field in the easy plane; b) at 45° of the easy plane and c) along the hard axis.

A resonance at the corresponding field strength. One obtains:

$$H^2_r = H_0^2 \frac{H_0^2 - H_+^2}{H_0^2 - H_+^2 \sin^2 \phi}$$

where $H_0 = \omega_0' \gamma$ is the resonance field in the easy plane. There are clearly two cases, according to the value of $H_0$ compared to $H_+$. The corresponding rotation patterns are
Fig. 13. — Corresponding normalized resonance field rotation patterns, rotating the field in a plane containing the $\bar{3}$ axis. The angle origin is chosen for the field along the $\bar{3}$ axis direction. Two situations are distinguished: a) $H_+ > H_0$, b) $H_+ < H_0$.

schematized in figure 13. In particular, a quasi-sinusoidal pattern is obtained when $H_+ < H_0$.

The fit given in figure 11a is obtained with the above formula of the resonance field. Although $H_+$ is quite small ($H_+ = 2.03$ kG), a small improvement of the fit from a sinusoidal dependence is already visible.

The theory of the AF linewidth is much less elaborated [9]. There is a simple argument that predicts $\Delta H \sim (\partial \omega / \partial H)^{-1}$ (where $\omega$ is the frequency of the relevant mode). However, the
prefactor can be anisotropic and in fact can play a role in the present case where no drastic \( \phi \) dependence exists. Thus we shall not attempt to give a quantitative explanation for the data of figure 11b.

b) Salts of the molybdenum series: Let us now consider \((\text{TTF}^{+})_3(\text{Mo}_6\text{Cl}_{14}^{2-})(\text{Cl}^-)\), representative of the molybdenum series. The data given figure 9a show that the degeneracy previously observed in the easy plane is now weakly removed. Since the two \( \text{Cl}/\text{Cl} \) salts have very similar structures, any explanation based on the nature or organization of the TTF molecules can be ruled out. The most plausible origin of this difference is a different magnetic superstructure which would break the rhombohedral symmetry in the molybdenum series of salts. A discussion of the expected superstructure is given in the next section. In any case, the symmetry of the paramagnetic phase will imply the presence of three equivalent solutions for the magnetic ordering, i.e., three equivalent AFMR signals. This is exactly what is shown in figure 9a where the translation of 60° between the three components is now readily understood. Considering one of these signals, figure 9a reveals the existence of a finite spin-flop field, i.e. gives the rotation pattern in the easy-intermediate plane. The fit to the data should therefore be considered in the most general case of orthorhombic magnetic anisotropy as described by Nagamiya [9]. Although the general treatment of the resonance becomes more complicated, the situation where the easy/intermediate anisotropy is weak can be deduced from the uniaxial case. One needs to introduce another parameter \( H_- \) related to the anisotropy in this plane. Analytic formulae are available for rotations in simple planes.

- in the easy/intermediate plane one gets:

\[
H^2_r = H^2_0 + H^2_- \cos 2 \theta
\]

where \( \theta \) is the angle between the magnetic field and the easy axis.

- for rotations in the easy/hard or easy/intermediate planes, one can deduce:

\[
H^2_r = H^2_0 \left( \frac{H^2_0 - H^2_+}{H^2_0 - H^2_- \sin^2 \phi} \right)
\]

where \( \phi \) is the angle between the magnetic field and the hard axis. \( H_0 \) and \( H'_+ \) are effective parameters which read

\[
H^2_0 = H^2_0 + H^2_- \quad , \quad H'_+ = H_+ \quad \text{for the easy/hard rotation}
\]

\[
H^2_0 = H^2_0 - H^2_- \quad , \quad H^2_- = H^2_+ - H^2_- \quad \text{for the intermediate/hard rotation}.
\]

We now use these results to analyse our results.

From results of figure 9a, we deduce that the AFMR corresponding to a single magnetic domain follows in fact the \( \theta \) dependence predicted by the theory since the rotation pattern for \( H_r \) becomes quasi-sinusoidal for small values of \( H_- \). The experimental parameter \( h \) is related to \( H_- \) by : \( H_0 + h = \sqrt{H^2_0 + H^2_-} \) which gives \( H_- \leq 850\text{-}1000 \text{ G} \) for the \( \text{Cl}/\text{Cl} \) salt. Similarly, the continuous lines given in figures 9b and 10 were obtained by fitting the data with the uniaxial symmetry and effective parameters.

The deduced values of these parameters are reported in table II. As expected, the smallest \( H^2_0 \) corresponds to the smallest \( H'_+ \). In addition, if these values of \( H'_+ \) are taken as the extrema of this effective parameter, one gets the values for \( H_+ \) and \( H_- \) reported in table II. Note that because of the lack of separation of the different components, only \( H_+ \) was determined for the \( \text{Br}/\text{I} \) salt. Note also that because of the exact in-plane degeneracy for the rhenium phase \( \delta \), there is no finite spin-flop field, i.e., \( H_- = 0 \) (Tab. II).
The analysis of the data in table II also indicates that $H_+$ and $H_-$ decrease with $T_N$, a trend consistent with the AFMR theory [9] and earlier experimental results [7b]. In addition, for 1 and 2, with identical $T_N$, one observes that $H_+$ and $H_-$ are similar, which points out to a common origin for the magnetic anisotropy. Moreover, the qualitative difference of the rotation patterns as for example in figures 9 and 11, is now readily understood by considering the magnitude of $H_+$. When $H_+$ is larger than 3.300 G (compounds 1, 2 and 3), a pseudo-parabolic pattern is obtained. Conversely, a quasi-sinusoidal rotation pattern is found for 4 and 5.

We now discuss in more details the linewidth rotation pattern given in figure 9c. As previously, we simplify the presentation, considering the uniaxial case with effective parameters. We start from the expression of the linewidth:

$$\Delta H = \Delta H_0 \left( \frac{d(\omega/\gamma)}{dH} \right)^{-1}$$

which gives in the uniaxial case:

$$\Delta H = \Delta H_0 \frac{H_0^4 - 2 H_0^2 H_+^2 \sin^2 \phi + H_+^4 \sin^2 \phi}{(H_+^2 \sin^2 \phi - H_0^2)^{3/2} (H_+^2 - H_0^2)^{1/2}}.$$

The continuous line in figure 9c gives a fit to this function with $\Delta H_0 = 46$ G and $H'_* = 4.9$ kG ($H_0$ deduced from the resonance field rotation pattern was fixed at 3.24 kG). Considering that we have omitted the angular dependence of $\Delta H_0$, in the above formula the agreement is excellent, thereby providing an independent test of the AFMR theory.

5. Brief discussion of the origin of the structured AFMR signal. — In the preceding section, each of the three components was considered as a single line. However, it is shown in figure 8 that they are in fact composite signals. This result, together with the fact that the degeneracy is broken in the plane perpendicular to the $\bar{3}$ axis suggest the occurrence of complex magnetic superstructures. Clearly, the high, rhombohedral crystal symmetry is lost in the magnetic phase for the molybdenum compound 5. Likewise, one observes that the degeneracy is preserved in the rhenium cluster compound 5 which implies a simpler, commensurate magnetic superstructure.

Preliminary calculations of the intermolecular transfer integrals between TTF molecules indicate that the largest intermolecular interactions occur between TTF of neighbouring planes (see Fig. 1 and Ref. [1a]). Smaller interactions are found between nearest molecules into a single plane. Both types of interactions lead to antiferromagnetic exchange in the localized limit relevant for the present insulating samples.

The situation with interplane interactions only is very simple. The magnetic energy is minimized for ferromagnetically ordered planes, antiferromagnetically coupled along the $\bar{3}$ axis. This simple commensurate magnetic superstructure, readily described in hexagonal symmetry, preserves the degeneracy within the easy plane. We expect this superstructure to remain the most stable for small intraplane interactions and we suggest that this situation corresponds to (TTF$^+$)$_3$(Re$_8$S$_6$Cl$_8^-$)(Cl$^-$), 5.

Larger in-plane interactions can complete with the interplane exchange and lead to a frustrated situation. In this case we expect a more complicated superstructure, in general incommensurate with the underlying lattice, which breaks the three fold symmetry and leads to an easy/intermediate anisotropy. We suggest that this situation is found in the molybdenum series although a detailed determination of the magnetic interactions is still missing in order to confirm this argument. In any case, the weak value of $H_-$ indicates that the latter salts remain close to the simple commensurate case. In the following, we essentially discuss the value of
$H_\perp$ (the easy/hard anisotropy) assuming ferromagnetically ordered planes stacked antiferromagnetically. A more sophisticated discussion of the magnetic anisotropy is left for a future publication.

The anisotropy between the easy plane and the hard axis can be estimated by the technique already used for other TTF-based radical cation salts [8, 10]. The room temperature crystal structure of the Cl/Cl molybdenum salt 1 has been used. The result should be representative of the whole series since the anisotropy tensor is known to be weakly dependent on small modifications of the crystal structure, once the magnetic superstructure is fixed [8, 11]. The spin is distributed over the TTF molecules, using the spin density obtained for TTF$^+$ from molecular orbital calculation. The anisotropy is calculated from:

$$E_a = \sum \sum \rho_i \rho_j \left( \frac{\mu_{i1} \mu_{jn} - 3 \mu_{i1} \cdot u_{ij}^n \mu_{jn} \cdot u_{ij}^n}{(R_{ij}^a)^3} \right)$$

where $\rho_i$ is the spin density on the atom $i$ of the TTF. The index $n$ labels the molecules. $u_{ij}^n$ is the unit vector for the direction between the atom $i$ of molecule 1 and the atom $j$ of molecule $n$. $R_{ij}^a$ is the corresponding distance. To insure the convergence of the series, the sum was extended over $n$ TTF molecules inside a sphere of a radius of five interplane separations.

We have estimated the anisotropy when the direction of the magnetic moments is respectively along and perpendicular to the 3 axis. The larger energy is found in the former case, confirming the existence of an easy plane (hard axis). The anisotropy between the two numbers is $\Delta E_a = 4.5 \text{ mK}$, which is very similar to the result already obtained in TTF based cation radical salts. This energy can be transposed in terms of anisotropy field $H_\perp$ which reads:

$$H_\perp = \frac{1}{\mu_B} \sqrt{\frac{4J}{\Delta E_a}}$$

where $\mu_B$ is the Bohr magneton. $J$ is the mean field exchange energy which enters in the spin wave theory. Independently of the details of the magnetic interactions, an estimate of $J$ is given by the Curie-Weiss temperature deduced from the magnetic susceptibility in the paramagnetic state. Taking $\theta_{\text{CW}} = 13 \text{ K}$ as a typical value among the series, we obtain $H_\perp = 7200 \text{ G}$. This is in good agreement with experimental results, considering that this calculation is the absolute zero limit (for a saturated order parameter). At a finite temperature, the expected anisotropy field is [9]:

$$H_\perp(T) = H_\perp(0) M$$

where $M$ is the order parameter (magnetization of a sublattice). The experimental value $H_\perp(4.5 \text{ K}) = 5300 \text{ G}$ for the Cl/Cl salt leads to $M = 0.74$ which is quite reasonable for $T/T_N \approx 0.5$. In the same way, the smaller value of $H_\perp(4.5 \text{ K})$ found for other salts of the series (see Tab. II) is clearly correlated to a smaller Néel temperature and our data suggest the same origin of the anisotropy among the series.

Conclusion.

In summary, this unique series of molecular perovskites offers an unprecedented opportunity for a detailed, quantitative comparative discussion of the electronic magnetic resonance properties of cation radical salts.

In the paramagnetic regime, the sensibility of the EPR linewidth to the sample preparation is a striking unusual result. This shows the importance of the spin-orbit coupling via the TTF.
environment. Nevertheless, the $g$ factor and EPR linewidth present a uniaxial symmetry consequence of the crystal structure. It is also found that the temperature dependence of the linewidth correlates with the nature of the halogen within the large cluster dianion.

The most distinctive results were however obtained below the magnetic ordering through an antiferromagnetic resonance study. For the first time, the high crystal symmetry allows for a detailed, comprehensive study of the rotation patterns for the resonance field and AFMR linewidth. The shape of the resonance signal is shown to be a composite line for most of the samples. In addition, a comparison with the $\text{Re}_2\text{S}_2\text{Cl}_6^-$ salt allows an unprecedented discussion of these complex features. In this respect, the significance of complex AFMR signals observed previously in other families of TTF-based cation-radical salts has been essentially overlooked and can now be addressed properly in the light of the present results.

Extension of this work will include the synthesis and study of other molecular perovskites. In particular, we plan to synthesize alloys mixing the two types of clusters in order to correlate more precisely the magnetic properties to the evolution of the crystal structure. Finally, magnetization measurements at a low magnetic field are in progress to specify the behaviour around the estimated spin-flop field.

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**References**

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