# Synthesis and Magnetic Properties of New Chromium(III)-Acetylide-TTF Type Complexes

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## 1. Introduction

Previously, we reported a promising magnetic properties of \([\text{CrCyclam(C≡C-MeEDT-TTF)}]^{[3]}\) (Fig. 1). In the oxidation state of the complex, the magnetic moment of Cr³⁺ \((S = 3/2)\) strongly interacts with those of the TTF ligands \((S = 1/2)\), while the latter can bring the strong inter-molecular exchange interaction through π-stacking.

Here, we report the synthesis of new Cr(III)-acetylide-TTF type complexes, \([\text{CrCyclam(C≡C-MeEDO-TTF)}]^{[2+]}\) and \([\text{CrCyclam(C≡C-MeBMT-TTF)}]^{[3]}\). The highly soluble functional groups of the complexes (ethylenedioxy and thiomethyl) make it easy to construct molecule-based magnetic materials. We also report the crystal structures and the magnetic properties of the crystals containing the complexes.

## 2. Synthesis and CV measurements

### Synthesis

\[
\text{Cyclic Voltammetry} \\
V/V: 0.25 \text{ mM, 0.1 M (Bu}_4\text{N})\text{ClO}_4, \text{acetonitrile, Ag/Ag}^+, 100 \text{ mV/s}
\]

\[
\text{Reversible oxidation of TTF units}
\]

### Cyclic Voltammetry

\[
\text{Fig. 1. The molecular structures of Cr-acetylide-TTF type complexes.}
\]

## 3. Crystal structures and magnetic Properties

\[
\text{[CrCyclam(C≡C-MeBMT-TTF)}]^{[2]}(\text{ClO}_4)_{[3]}(\text{PhCl})_2 \\
\]

\[
\text{Ferrimagnetic chain of [CrCyclam(C≡C-MeBMT-TTF)}]^{[2]} \\
\text{Delocalized spin (canted)}
\]

\[
\text{[CrCyclam(C≡C-MeEDO-TTF)}]^{[2]}(\text{ClO}_4)_{[3]}(\text{PhCl})_2(\text{H}_2\text{O})_2 \\
\]

\[
\text{Ferrimagnetic chain of [CrCyclam(C≡C-MeEDO-TTF)}]^{[2]} \\
\text{Delocalized spin (canted)}
\]

\[
\text{[CrCyclam(C≡C-MeEDT-TTF)}]^{[3]}(\text{ClO}_4)_{[2]}(\text{PhCl})_2(\text{H}_2\text{O})_2 \\
\]

\[
\text{Strong intra-chain interaction (2J / k_B} = -28 \text{ K)}
\]

\[
\text{Isolated [CrPhen(NCS)}]^{[4]} \\
\text{(Exchange interaction is negligible)}
\]

## 4. Conclusion

Two new Cr-C≡C-TTF type complexes were synthesized.

The \([\text{CrCyclam(C≡C-MeEDO-TTF)}]^{[2]}\) salts are characterized by the ferrimagnetic chain of the complex with the strong intra-chain interaction of \(2J / k_B = -28 \left(\text{[CrPhen(NCS)}]^{[4]}\right)\) and -24 K \((\text{ClO}_4)\).

\([\text{CrCyclam(C≡C-MeBMT-TTF)}]^{[2]}(\text{ClO}_4)_{[2]}(\text{PhCl})_2(\text{H}_2\text{O})_2\) shows a weakferromagnetic transition at 21 K.

Cr-C≡C-TTF type complexes are promising for molecule-based magnetic materials owing to the strong intra- and inter-molecular interaction through the ethynyl group and the π-stacking of TTF-ligands, respectively.