Synthese and magnetic properties of new polymetallic complexes of coordination.

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Introduction:
definition of the photomagnetism by electron transfer.

I. Photomagnetism of a 3D network: Cu$^{II}_2$[Mo$^{IV}$(CN)$_8$.7,5H$_2$O
1) Presentation.
2) Photomagnetic cycles at 60 K, tests of relaxations.
3) Photomagnetic cycles at 10 K.

I. Photomagnetism of a new cluster: [Cu$^{II}$(tren)]$_6$[Mo$^{IV}$(CN)$_8$][ClO$_4$]$_8$.16H$_2$O
1) Presentation.
2) Description of the photomagnetic effect.

III. Study of relaxation.
1) Tests of follow-up of the magnetic signal versus time at a given T.
2) Study of relaxation by thermal cycles.

Conclusions

Project of thesis
Under the direction of Prf Maria Vaz (iq-ufrj) and Prf Miguel Novak (if-ufrj)
new compounds with interesting magnetic properties.
Introduction

Definition of the photomagnetism:

influence of an electromagnetic irradiation on the magnetic properties of a material
Possible mechanisms on a molecular scale:

- Spin transition, centered on the metal: example of the Fe($^\text{II}$)($^d_6$)

  \[
  \begin{align*}
  \text{LS} & : S = 0 \\
  \text{HS} & : S = 2
  \end{align*}
  \]

  \[
  \begin{align*}
  \text{e}_g & \\
  \text{t}_2g &
  \end{align*}
  \]

- Electronic transfer: example of the Rb$_{0.54}$Co$_{1.21}$[Fe(CN)$_6$].17H$_2$O

  \[Fe^{\text{II}}\text{-CN-Co}^{\text{III}}\]

* A. Bleuzen, M. Verdaguer, JACS, 2001, 122, 6648.
Photomagnetism of a network 3D: \( \text{Cu}^{\text{II}}_2\text{[Mo}^{\text{IV}}(\text{CN})_8] \cdot 7,5\text{H}_2\text{O}\) *

1) Presentation

IVCT à 450 nm

Irradiation 5 h in 60 K:
(power of the laser \( \approx 3 \text{ mW.cm}^{-2} \))

\[ \chi_M T \text{ (cm}^3\text{.mol}^{-1}\text{.K)} } \]

- befor \( \hbar V \)
- after \( \hbar V \)
- after \( \hbar V \) and annealing in 300 K

the curves befor and after irradiation meet in 180 K.

the curves befor and after irradiation + thermal annealing are identical.
2) Magnetic cycles in 60 K, tests of relaxations.

Irradiations in 60 K

- the 4 irradiations are effective
  - no fatigability of the process of photo-conversion

- 160 K: incomplete relaxation
- 180 K and 200 K: relaxations at the same point, but not complete
  - surprising bad reversibility
  cf. courbe $\chi T = f(T)$
3) photomagnetic cycles at 10 K.
Irradiation 1 h at 10 K

\[ \chi_T \approx 0.14 \text{ cm}^3\text{mol}^{-1}\text{K} \]

\( \chi_T \) after annealing \( \approx \chi_T \) before \( h \nu \)

- \( \Delta \chi_T \approx 0.14 \text{ cm}^3\text{mol}^{-1}\text{K} \)
- \( \chi_T \) after annealing \( \approx \chi_T \) before \( h \nu \)

non fatigability

good reversibility
Conclusions of the 1st part:

Conditions of good reversibility: \( h \nu \) 1 h in 10 K

in this case: the photo-conversion obtained is insufficient to study of relaxation

notice: the xT curve obtained after irradiation looks like that obtained for compounds organized in clusters

→ Idea: to obtain systems organized in clusters
   - with a more important photomagnetism
   - allowing a simulation of magnetic properties

\[ \text{Coord}_{\text{Mo}} = 8 \]

ideal stoechiometry: 1 Mo / 8 Cu

This compound does not exist

but the compound 1 Mo / 6 Cu was synthesized by the group of Pr. Michel Verdaguer
Photomagnetism of a new cluster: 
$[\text{Cu}^{II}(\text{tren})]_6[\text{Mo}^{IV}(\text{CN})_8][\text{ClO}_4]_8 \cdot 16\text{H}_2\text{O}$

1) Presentation

**ligand tren**

![Diagram of the cluster complex]

- $\text{Cu}^{II}$
- $\text{N}$
- $\text{Mo}^{IV}$
- $\text{C}$
2) Description of the photomagnetic effect.

- Irradiation (406 nm) à 10 K

\[
\chi_{MT} = 2.3 \text{ cm}^3\text{.mol}^{-1}\text{.K}
\]

before irradiation

after irradiation 15 h at 10 K

after irradiation + annealing à 300 K

\[ M_{\text{before } h} \approx M_{\text{after } h + \text{annealing}} \]

Reversibility of the photo-induced process

\[ \Delta \chi T = 2.3 \text{ cm}^3\text{.mol}^{-1}\text{.K} \]

Photomagnetic effect important
- short irradiation in 10 K, non-fatigability of the process

before irradiation
simulation « 6 S=1/2 »

after irradiation 1 h à 10 K
sim. 57 % « S=3 » + 43 % « 6 S=1/2 »
simulation « S=3 »

Reversibility and no fatigability of a photo-induced process

good candidate for the study of the relaxation
study of the relaxation

1) Tests of follow-up of magnetic signal versus time with $T$ given.

at each temperature tested, stability of $x_T$ ⇒ relaxation during the increase in $T$?
2) Study of relaxation by thermal cycles.

Relaxation from a cycle to the following

Points of meeting • at the end of each cycle

relaxation takes place during the increase in the $T$
relaxation during the 1st passage only

\[ \hbar \nu \]

\[ 406 \text{ nm} \]

\[ T (\text{K}) \]

\[ 10 \text{k} 100 \text{k} 150 \text{k} 200 \text{k} 250 \text{k} 300 \text{k} \]

\[ \chi_M (\text{cm}^3 \text{mol}^{-1} \text{K}) \]

\[ H = 20000 \text{ Oe} \]

- After each increase in the T, the signal is stable
- Creation of magnetic centers with a distribution of \( T_{\text{relaxation}} \)

\[ \hbar \nu_1 \]

\[ A \leftrightarrow B_1 + B_2 + B_3 \ldots \]

\[ \Delta_{B_1}, \Delta_{B_2}, \Delta_{B_3} \ldots \]
Conclusions

3D network Cu\textsubscript{2}Mo: photomagnetism reversible (h\nu 1 h à 10 K), but too weak photoconversion

To increase the efficacy of the irradiation:
- approach top-down: nano-materials
  (too small quantities for the moment)
- approach bottom-up
  → analogy with the molecular clusters

Cluster Cu\textsubscript{6}Mo: - photomagnetism reversible and important,
  but relaxation non-conventional: independent of the time.
  - stability of the signal with T given.

\[ \begin{align*}
  &A \xrightarrow{\text{hv}} B \xrightarrow{\text{annealing with } T_1} B^* \\
  &\text{annealing with } 300 \text{ K}
\end{align*} \]

Example: \( T_1 = 150 \text{ K} \)
\( \Delta \chi T = 1,1 \text{ cm}^3\text{mol}^{-1}\text{K} \)