Experimental report

21/05/2024

Proposal: 5-51-592 **Council:** 10/2022

Title: Determination of the magnetic anisotropy axes of a new Cr10 wheel compound

Research area: Physics

This proposal is a new proposal

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Samples: Cr5C15O20H35
C10 H9 N Fe Cl5

Instrument	Requested days	Allocated days	From	To
D19	4	5	03/04/2023	08/04/2023
D3 High field >1T	7	7	11/05/2023	18/05/2023

Abstract:

Our research group has successfully synthesized single crystals of a new member of the wheel family of Cr10 compounds based on methoxy and formate (HCOO-) anions.
Magnetization shows that XT at room temperature is consistent for ten uncoupled paramagnetic centers with S = 3/2 (19 emu K mol-1). When the temperature decreases, the XT product slightly increases until 50 K, when the increase is more abrupt, reaching a maximum at 18 K, then dropping suddenly. To understand this complex magnetic data, we performed DFT calculations of J. These results led to a model of two sets of ferromagnetic chromium cations connected by two cations in an asymmetric antiferromagnetic coupling, achieving a ground state of S = 9.
To complete this study, we are currently working on magnetic anisotropy calculations that would be perfectly complemented with polarized neutron diffraction to understand the role of this property in the magnetic model we are proposing

Determination of the magnetic anisotropy axis of a new Cr_{10} wheel compound

In the field of molecular magnetism, the wheel kind of compounds have turned quite interesting due to their particular magnetic nature, which has afforded them to become attractive candidates as materials for information processing at quantum level. This is due to their high symmetry and planar character of these systems, which confers them the possibility to deposit on substrates and surfaces, a key process of device manufacture[1].

In this sense, wheel compounds based on Cr^{III} cation and carboxylate ligands are remarkable examples. It's been reported that, in these systems, the carbonated chains play a crucial role in the observed magnetic properties, allowing to have better tools at the time of designing these structures and predicting their magnetic behaviour, which is typically antiferromagnetic[2].

Low et al[3], in 2006, reported the magnetic study of a family of chromium-based wheel compounds, with a general formula of $[Cr_{10}(RO)_{20}(R'COO)_{10}]$, obtained only by solvothermal conditions. Herein, the authors present 4 compounds with R/R' = CH_3/CH_3CH_2, CH_3CH_2/CH_3CH_2, $CH_3/(CH_3)_3C$, $CH_3CH_2/(CH_3)_3C$ and study the influence of the organic chains in the crystal packing of the species and therefore, in the magnetic behaviour. They stated that methoxy (CH_3O) bridges would generate more ferromagnetic coupling than the ethoxy (CH_3CH_2O) analogues, being not able to explain the mechanism at that time. Also, they conclude that even though the antiferromagnetic interaction, evidenced by M(T) measures, should lead to a ground state with S = 0, Inelastic Neutron Scattering (INS) data for deuterated samples were more consistent with a S = 15 ground state for three of the compounds and a large value of S for $[Cr_{10}(CH_3O)_{20}((CH_3)_3CCOO)_{10}]$ compound. This left the question of what the true nature of the magnetic interactions in these systems is.

The last year, Rubín et al[4]. reported an exhaustive magnetic analysis for the latter compound, revealing that it has an unusual ground state of S = 9 which has its foundation on a coupling model of two semi-crowns of four FM coupled Cr^{III} ions separated by two Cr^{III} cations AFM asymmetrically coupled.

Now, our research group have successfully synthesised single crystals of a new member of the wheel family of Cr_{10} compounds, based of methoxy and formate anion ($HCOO^-$). This compound happens to be the most condensed system because both organic ligands are the simplest and smallest of each kind, generating intermolecular plane distances in the range of 6.7879 – 7.2957 Å, being 7.74 Å the shortest distance previously reported for $[Cr_{10}(CH_3O)_{20}(CH_3CH_2COO)_{10}]$. The wheels possess a stacking fashion of packing, and the direction of the stacking is completely parallel to the shortest cell axis (*a*).

From the magnetic point of view, iso-field magnetisation shows that $\chi_M T$ at room temperature is consistent for ten uncoupled paramagnetic centers with S = 3/2 (19 emu K mol^{-1}). When the temperature is decreased, the susceptibility-temperature product slightly increases until 50 K, when the increasing is more abrupt reaching a maximum at 18 K, to then decrease suddenly. To understand

this complex magnetic data, we performed DFT calculations of *J*, obtaining similar results as the reported by Rubín et al, which lead to a model of two sets of ferromagnetic chromium cations connected by two cations in an asymmetric antiferromagnetic coupling, achieving a ground state of S = 9.

To complete this study, we are currently working in magnetic anisotropy calculations that would be perfectly complemented with neutron scattering measures to understand the role this property in the magnetic model that we are proposing.

Therefore, the goal of this proposal is the determination of the **magnetic anisotropy axis** for each one of the 5 Cr cations in the asymmetric unit of the compound $[Cr_{10}(CH_3O)_{20}(HCOO)_{10}]$, by using polarised neutron diffraction in single crystal.

Considering the lattices parameters of these compounds, ranging between 7 and 27 Å, we consider that D19 will be the instrument to refine the nuclear structure at low temperature and D3 the one for collect data with up and down neutron polarizations. The crystals have sizes of approximately 1 x 0.3 x 0.3 mm.

For the D19 experiments we apply for 4 days in order to collect one sets of data at low temperature (5K), with the help of the displex cryo-cooler. The set of data must be complete enough in order to allow the refinement of the nuclear structures. At D3 the intensity of a set of Bragg lines will be measured for both neutron polarizations during 5 days.

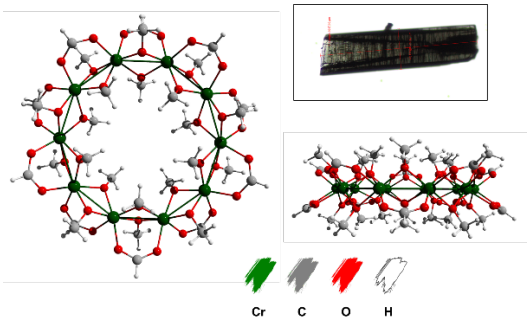

Figure 1. Parallel and perpendicular view for the new Cr_{10} wheel compound with a inset photo of a single crystal.

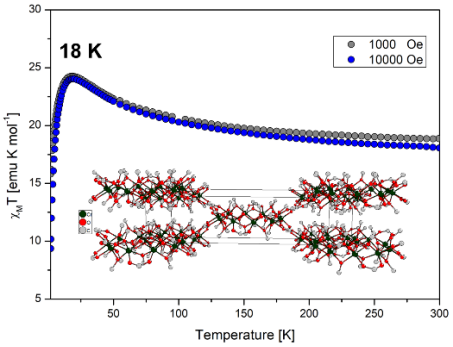

Figure 2. $\chi_M T(T)$ plot at 1000 and 10000 Oe with a picture of the packing of the Cr_{10} wheel compound.

References

1. Troiani, F. *et al.* Molecular engineering of antiferromagnetic rings for quantum computation. *Phys. Rev. Lett.* **94**, 1–4 (2005).
2. McInnes, E. J. L. *et al.* Solvothermal synthesis of [Cr10(μ-O2CMe)10(μ-OR)20] 'chromic wheels' with antiferromagnetic (R = Et) and ferromagnetic (R = Me) (Cr(III)···Cr(III). *Chem. Commun.* **10**, 89–90 (2001).
3. Low, D. M. *et al.* A Family of Ferro- and Antiferromagnetically Coupled Decametallic Chromium(III) Wheels. 1385–1396 (2006) doi:10.1002/chem.200501041.
4. Rubín, J. *et al.* Origin of the Unusual Ground-State Spin S = 9 in a Cr10 Single- Molecule Magnet. *J. Am. Chem. Soc.* (2022) doi:10.1021/jacs.2c05453.

Experiments.

Unfortunately, the size and crystallinity of the samples was not enough in order to allow a collection of data at D19. Therefore, the experiment was cancelled.