

## Crystal and Magnetic structures and Dielectric phase transition of the novel Organic-Inorganic Hybrid Halometallate compound: (quinuclidine)[FeCl<sub>4</sub>]

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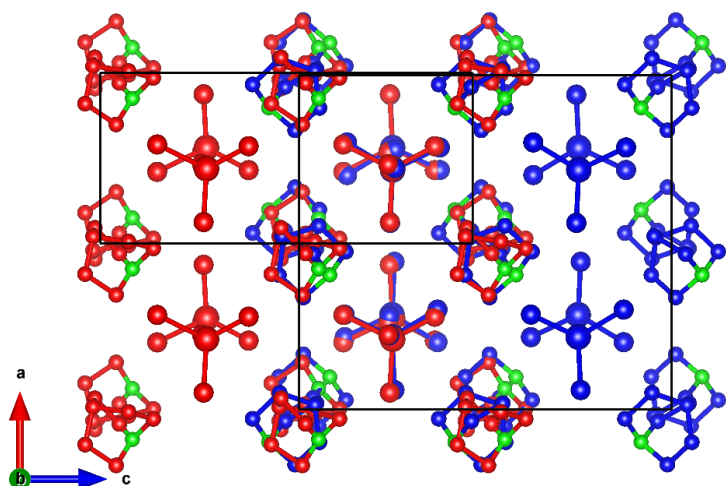
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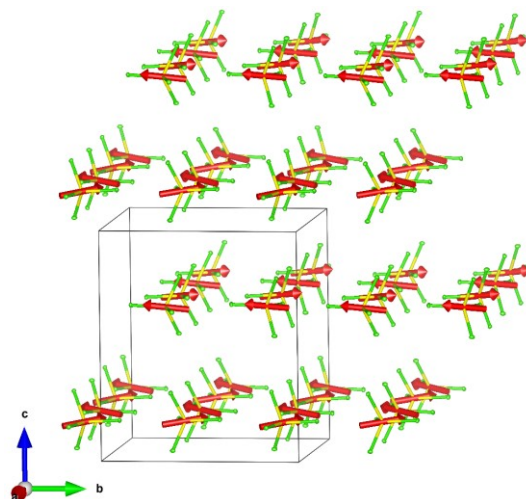
The synthesis of multifunctional materials is a hot focus of research in materials science. In this respect, the synthesis of complexes based on the combination of organic-inorganic building blocks provides a promising approach in the design of systems with tuneable properties. In this communication we will present the properties of a new compound based on quinuclidine as the organic cation and FeCl<sub>4</sub> as the inorganic anion, with the formula (quinuclidine)[FeCl<sub>4</sub>]. Similar compounds derived of this heterocyclic cation have been found to present interesting ferroelectric properties.[1] In this context, the multifunctional behaviour of this novel molecular crystal is related to the electronic structure of the 3d<sup>5</sup> configuration of the Fe(III) ions together with the ability of the counter-ions to change of orientation or even become disordered as a function of temperature.

The structural characterization of (quinuclidine)[FeCl<sub>4</sub>] compound shows two phase transitions. The first one, detected in the range from 100 to 300 K, was resolved by single-crystal X-Ray and neutron diffraction. At 300 K, the compound presents the orthorhombic space group *Pbc*2<sub>1</sub>. At 100 K, the space group is *Pbca*, with a doubling of the *a*-axis, related to the rotation of the cations: two different orientations of the counterion are observed in the low temperature phase along the *a* direction, contrary to the high temperature phase, where it appears only one orientation.

Moreover, this compound presents long-range magnetic order below 3 K. The magnetic structure was solved using single-crystal and powder neutron diffraction data from D19 and D1B instruments (ILL, France), respectively. Our best model was found on the Shubnikov magnetic space group *P*2<sub>1</sub>'2<sub>1</sub>'2<sub>1</sub>. Although the refined model present an antiferromagnetic structure, based on the symmetry analysis of the *P*2<sub>1</sub>'2<sub>1</sub>'2<sub>1</sub> Shubnikov group, a ferromagnetic component along the *c* direction is allowed. However, the refinement of this ferromagnetic component is beyond the precision of our measurements. Nevertheless, this can be fixed to the values derived from the macroscopic magnetometry measurements (SQUID). In order to provide a complete model these values were included in the magnetic model and fixed during the refinements.

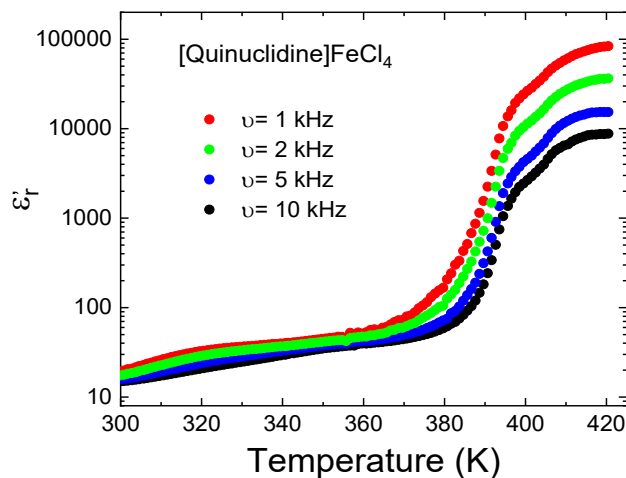


**Figure 1:** Unit cell of (quinuclidine)[FeCl<sub>4</sub>] at 10 K (blue) and 295 K (red). The nitrogen atoms are shown in green and the hydrogen atoms have been omitted for the sake of clarity.



**Figure 2:** Magnetic structure of (quinuclidine)[FeCl<sub>4</sub>] at 1.8 K. Color codes: yellow, iron; green, chloride; red, magnetic spin. The organic cations have been omitted for the sake of clarity.

At temperatures higher than R.T, there is a second structural phase transition which produces an important modification of the electric behaviour, as it has been reported on similar compounds.[1] The dielectric permittivity data collected shows a sharp phase transition around 390 K (also observed in DSC measurements). The value of the permittivity increases drastically with the increase of the temperature, reaching a maxima of  $10^5$  at 390 K (measured at 1 kHz). This value is notable larger than similar compounds of this family.[1] This interesting behaviour could be of interest for electrochemical applications.



**Figure 3:** Relative permittivity as a function of temperature for different frequencies, in the range 300-420 K. The measurements were taken applying an amplitude of 1 V to cold-press pelletized samples.

[1] (a) Jun Harada et al., *Nat Chem*, 2016 Oct; 8(10):946-52. (b) You-Meng You et al., *Nat Commun*. 2017, 8:14934. (c) Ting Fang et al., *Z. Anorg. Allg. Chem.* 2019, 645, 3-7. (d) Guang-Meng Fan et al., *CrystEngComm*, 2018,20, 7058-7061.

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