Poster

Incommensurate displacive and occupational modulation in the structures of $[Fe_xCr_{1-x}(urea)_6]$ $(NO_3)_3$ (x = [0, 1]) complexes

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Hexakis(urea-O)iron complexes with different anions have a multitude of applications, e.g. they are used as selective oxidants and catalysts in organic chemistry, nanocomposite materials, and fertilizers [1]. Despite being known for decades; the nitrate complex $[Fe(urea)_6](NO_3)_3$ lacks a proper structure description. We discovered that the structure of hexakis(urea-O)iron(III) nitrate is incommensurately modulated. The structure was refined in the $C2/c(\alpha 0\gamma)00$ superspace group with the modulation wavevector $\mathbf{q}$ = (−0.7692, 0, 0.9505). Up to the 3rd order satellite reflections were present in the diffraction data. This results in an anharmonic modulation as shown for the Fe(III) (Figure 1).

In addition to displacive modulation, there is a complex occupational modulation of the nitrate ions present. The nitrate ions form two disorder ensembles with three and two disorder components, respectively. The latter ensemble is situated at the two-fold axis that formally leads to four disorder components for this nitrate site. Despite the complex disorder, the unconstrained refinement in superspace results in a correct stoichiometry between the Fe(III) and the nitrate ions. The oxidation state of iron in this compound has been conclusively confirmed by Mössbauer spectroscopy measurements.

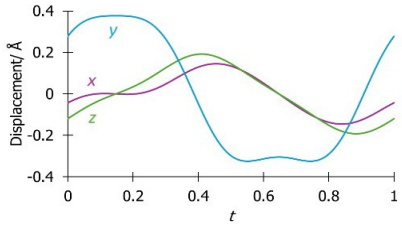

Figure 1. Displacement of the Fe(III) atom showing an anharmonic displacive modulation.

The compound forms solid solutions with Cr(III). The structure model of a 1:1 Fe(III):Cr(III) solid solution $[Fe_{0.5}Cr_{0.5}(urea)_6](NO_3)_3$ in $C2/c(\alpha 0\gamma)00$ with $\mathbf{q}$ = (−0.7649, 0, 0.9481) is also presented. Similar displacive and occupational modulation is found. The crystals containing Cr(III) ions display a strong dichroic effect (see Figure 2).

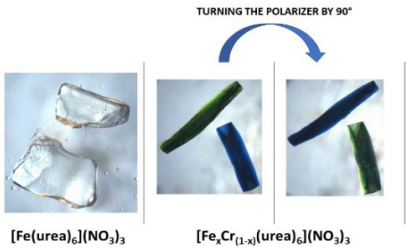

Figure 2. Pure hexakis(urea-O)iron(III) nitrate and the respective solid solution with Cr(III) displaying a strong dichroic effect.

[1] Béres, A. K., Homonnay, Z., Kótai, L. *ACS Omega* **2024**, 9(10), 11148–11167