


Experiment Report Form

	Experiment title: Temperature dependence of molecular symmetry in "Basic Metal(III) Carboxylates": a case of Magnetic Jahn-Teller Effect?	Experiment number: CH-3042
	Beamline: BM01A	Date of experiment: from: July 13 th 2010 to: July 17 th 2010
Shifts: 12	Local contact(s): Dr. Dmitry CHERNYSHOV	
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Report:

Introduction: The aim of this study was to investigate, by single-crystal diffraction experiments, eventual structural distortions, of "Basic Metal(III) carboxylates", $[M_3O(O_2CR)_6(L)_3]^+A^-$, as a function of temperature. For metal ions with half-integer spins (e.g. Fe^{III} , $S = 5/2$; Cr^{III} , $S = 3/2$) an equilateral Heisenberg-Dirac-van

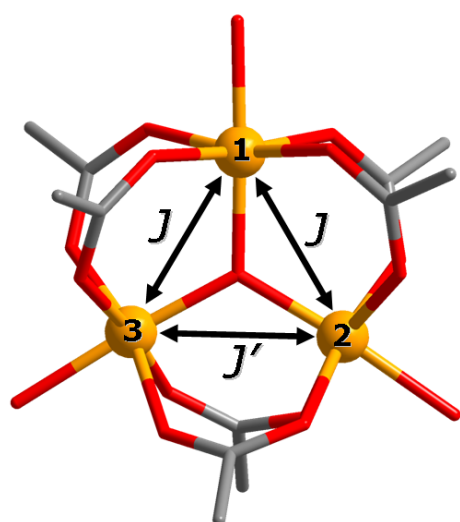


Figure 1. Structure of the cation $[M_3O(O_2CR)_6(L)_3]^+$ of basic metal(III) carboxylates

Vleck spin Hamiltonian ($J = J'$, Fig. 1) yields a doubly degenerate $S_T = 1/2$ ground state. However, low-temperature ($T < 20$ K) magnetic,¹ heat capacity² and EPR data³ can only be interpreted by assuming the lifting of this degeneracy, which can only be achieved by assuming that $J \neq J'$. Additionally, the interpretation of 1.5 K Inelastic Neutron Scattering (INS) data for $[Fe_3O(O_2CPh)_6(py)_3](ClO_4) \cdot py$ require the consideration of *two* separate Fe_3 complexes of C_{2v} symmetry,⁴ although its 233 K crystal structure reveals a crystallographically-imposed threefold symmetry. Therefore, this would suggest a structural symmetry lowering at low temperatures, in agreement with the "magnetic Jahn-Teller effect" (MJTE), proposed by Murao.⁵ Until now, all structural determinations of basic metal(III) carboxylates have been carried out above liquid-nitrogen temperatures, so their structural characteristics near liquid helium remain a matter of conjecture. We therefore wished to determine whether there is any low-T structural change in $[Fe_3O(O_2CPh)_6(py)_3](ClO_4) \cdot py$, a well characterized and stable compound. A second goal was to collect high resolution data at different temperatures and explore the probable variations in the charge density of carboxylate ligands or in the vicinity of metal ions.

Materials and Methods: In order to perform single-crystal studies at low temperatures we obtained machine time (12 shifts) at the BM01A line, one of the two SWISS -NORWEGIAN BEAM LINES. We used all time shifts, studying two crystals of $[Fe_3O(O_2CPh)_6(py)_3](ClO_4) \cdot py$, one placed in a capillary, and another glued on a glass fiber. The crystal in the capillary was placed in a closed-stream cryostat; low resolution data were

collected by cooling from room temperature down to 5K and then heating back to RT. Each measurement required approximately 45 min, and 24 data sets were collected in total. Above 20K the temperature was varied in steps of 20K and then in steps of 5K. From the crystal supported on the glass fiber two complete data sets (high and low resolution) were collected, one at RT and the other at 90 K under a nitrogen gas cryostream. All data collections were performed with a photon energy of 17.7 KeV (or 0.700476 Å).

Results. Cell variation: $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_3](\text{ClO}_4)\cdot\text{py}$ compound crystallizes in the $P6_3/m$ space group. The unit cell axes and volume at RT are: $a = 13.5285$ Å, $c = 19.1363$ Å and $V = 3033.11$ Å³. All the data sets were indexed based on a cell with hexagonal symmetry. Preliminary results of variable-temperature unit-cell refinements are shown in Fig. 2. As mentioned in the materials and methods section these data were collected using a He cryostat, the consequence of which is the limited access to reciprocal space. Taking into account the orientation of the crystal the most of the reflections with a component along c-axis are missing, and so the dispersion (and errors) of experimental points is larger for c-axis values. Although special care should be taken for the analysis of these measurements, the first important conclusion from this experiment is obvious: *no symmetry decrease is observed down to 5 K.*

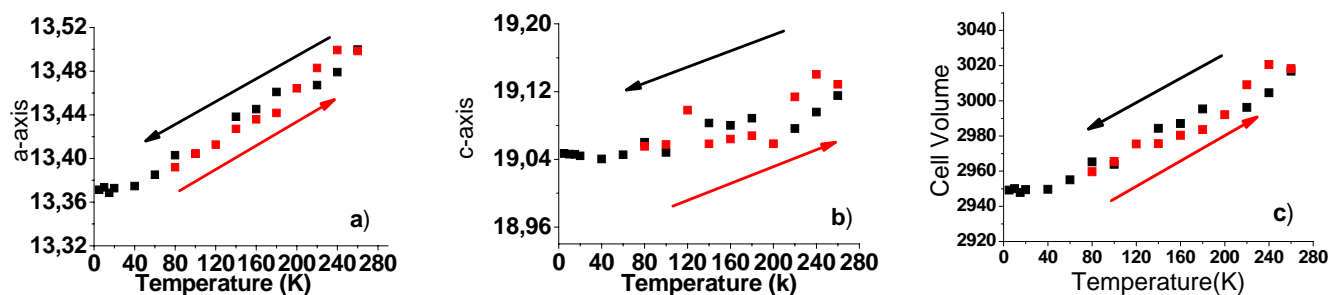


Figure 2. Cell parameter variation for $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_3](\text{ClO}_4)\cdot\text{py}$ as function of temperature. The black (red) point are the calculated values upon cooling (heating).

Charge density calculations: In order to better understand fine electronic effects that may influence the magnetic exchange within the cluster, we collected high-resolution diffraction data at 90 K and RT. The data were collected from a single crystal mounted on a glass fiber, inside a liquid nitrogen cryostream. Data redundancy was >9 for 85% of the reflections and data completeness up to $\theta = 35.970^\circ$ was 99%. Preliminary Fourier difference maps allow us to analyze the charge density distributions around the atoms of the complex. Fig. 3 shows such distributions around the benzoate ligand at 90 K. More detailed and rigorous analysis of these data is in progress.

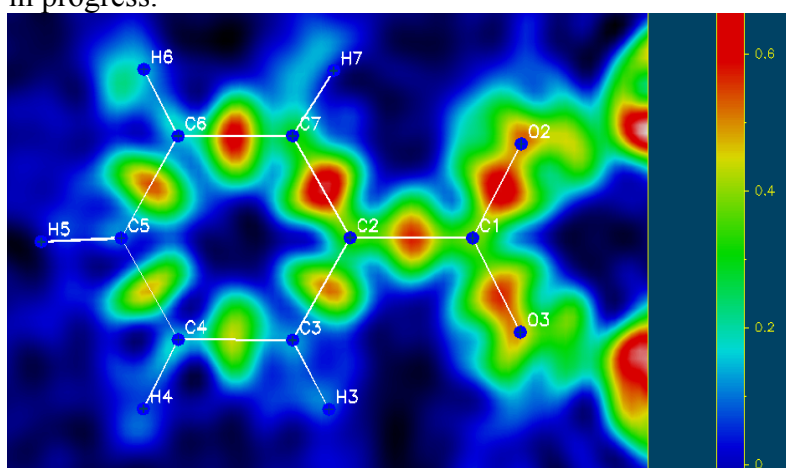


Figure 3. Residual density map for the benzoate ligand.

¹ (a) J. Wucher, J. D. Wasscher, *Physica*, 1954, 20, 361. (b) J. F. Duncan, C. R. Kanekar, K. F. Mok, *J. Chem. Soc. A*, 1969, 480.

² J. Wucher, J. D. Wasscher, *Physica*, 1954, 20, 721.

³ Y. V. Rakitin, Y. V. Yablokov, V. V. Zelentsov, *J. Magn. Res.* 1981, 43, 288.

⁴ F. E. Sowrey, C. Tilford, S. Wocadlo, C. E. Anson, A. K. Powell, S. M. Bennington, W. Montfroij, U. A. Jayasooriya, R. D. Cannon, *J. Chem. Soc., Dalton Trans.*, 2001, 862.

⁵ T. Murao, *Phys. Lett. A*, 1974, 49, 33.