ESRF

EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Photochemical linkage isomerization in single-crystals of $[Co(NH_3)_5NO_2]Br_2$ before and after a pressure-induced phase transition	**Experiment number**: CH-4908
Beamline:	**Date of experiment**: from: 22 Feb 2017 to: 25 Feb 2017	**Date of report**: 18 May 2017
Shifts: 9	**Local contact(s)**: Michael Hanfland (email: hanfland@esrf.fr)	*Received at ESRF:*

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Report:

The family of $[Co(NH_3)_5NO_2]XY$ photosensitive complexes gave rise to the broad field of research of photo- and thermo-mechanical effects in crystals. $[Co(NH_3)_5NO_2]Br_2$ is a unique member of this family in its response to hydrostatic pressure: it undergoes a single-crystal-to-single-crystal phase transition on increasing pressure. The structural distortion in the course of the phase transition was supposed to be able to affect the photoisomerization reaction $[Co(NH_3)_5NO_2]Br_2 \rightarrow [Co(NH_3)_5ONO]Br_2$, i.e. transformation from nitro- to nitrito-form. The aim of this project was to test this hypothesis and compare the structures of the $[Co(NH_3)_5ONO]Br_2$ linkage isomer: a) formed on irradiation of $[Co(NH_3)_5NO_2]Br_2$ by light at ambient pressure and then compressed in steps of ~1 GPa to 10 GPa, b) formed on irradiation of $[Co(NH_3)_5NO_2]Br_2$ by light at several pressure points before and after phase transition with ~1 GPa step up to 10 GPa.

To achieve this goal we have carried out two series of experiments. In the first series the initial nitro-isomer was transformed by light from a LED into a nitrito-isomer at ambient pressure, loaded into a diamond anvil cell using neon as pressure transmitting medium and diffraction from the sample was measured starting from ambient pressure up to 10 GPa with steps ~ 0.5 GPa. The crystals were found to be highly sensitive to X-ray beam of high intensity provided bu undulator at ID15B and data collection without radiation damage of the sample was possibe only with slightly unfocused beam providing 50-60 mkm spot size at the sample instead of 10 mkm. Continuous reversible phase transition in nitrito-form of the sample on increasing pressure has been found on increasing pressure. The structure of the high-pressure phase was successfully solved and refined. In the second series of experiments we tried to transform nitro- to nitrito-form by in situ irradiation of the sample by blue LED light in diamond anvil cell at different pressures. In the first run we have increased pressure in the cell with initial $[Co(NH_3)_5NO_2]Br_2$ sample above pressure transition point and found that for high pressure phase even continuous irradiation during 8 hours does not lead to formation of nitrito-isomer which can normally be obtained in 1 hour at ambient pressure. In the second run of experiments we have found that photoisomerization process stops even at pressures lower than phase transition point. At pressures close to phase transition point irradiation by blue light was preliminary found to influence the transition pressure. This assumption will be further considered after final data reduction and analysis.

The structures of $[Co(NH_3)_5NO_2]Br_2$ and $[Co(NH_3)_5ONO]Br_2$ were successfully solved and refined at different pressures. The results are now being analyzed and prepared for publication. The main result obtained from this experiment is a comparison of structural strain induced in the title compound by reaction initiated at high pressure, by pressure alone or by reaction alone. This will fill the gap in knowledge on the interrelation between pressure- and reaction-induced strain in the family of molecular and coordination compounds exhibiting photomechanical effects using $[Co(NH_3)_5NO_2]Br_2$ as successful model.