



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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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.



	Experiment title: The excited state structures of a luminescent Rhenium(I) N-heterocyclic carbene complex.	Experiment number: CH-910
Beamline: ID09	Date of experiment: from: 27/11/00 to: 3/12/00	Date of report: 1/3/02
Shifts: 15	Local contact(s): Michael Wulff, Friedrich Schotte, Toni Plech	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Jacqueline M. Cole, Department of Chemistry, University of Cambridge, UK. *Paul R. Raithby, Department of Chemistry, University of Bath, UK.		

Report:

The objective of this experiment was to establish the nature of the excited state of a rhenium(I) N-heterocyclic carbene in its solid state, using a stroboscopic pump-probe single-crystal diffraction technique. In essence the experiment involved performing two crystallographic structure determinations on the compound: one using conventional crystallographic methodologies that confirms the ground state structure, and the other using a laser pump-probe crystallographic method which is synchronised with the time-structure of the X-ray beam so that the excited state is activated in tandem with each X-ray measurement. This stroboscopic pump-probe method is required since the lifetimes of the emissive states of this class of compounds are of the order of μs . The materials are luminescent and emit principally from a metal-ligand charge transfer state. The subject compound, [HNCH₂CH₂NHCr(2,2'-bipyridine)(CO)₃]Br, is a key material in the initial part of a larger initiative that we are undertaking that aims to fully understand the excited state structural origins of luminescent materials. Armed with such knowledge, we will be able to suitably engineer and test close derivatives that have optimal band gap properties for application as light-emitting-diodes.

The choice of the subject material derives from its very favourable luminescent spectroscopic properties and its high symmetry (orthorhombic) compared with other compounds within this class of materials. This level of symmetry is essential since the measurements on ID9 need to be performed on a spindle axis and the level of reciprocal space coverage is thus largely restricted. This compound emits at a λ_{max} of 565 nm with a lifetime of 0.23 μs at room temperature. The lifetime is increased by 1-2 orders of magnitude on cooling to 20K since

spin-orbit coupling effects are enhanced. We therefore excited our crystal using a fs laser, at a $\lambda = 400$ nm (the closest high energy harmonic of the laser to the λ_{max} of the sample) and cooled our sample to the minimum possible ($T=77\text{K}$) using an Oxford Cryosystems Cryostream (an open-flow He cryostream was still being adapted for the beamline then and so was not available).

A crystal was mounted in perfluoroether and placed upon the phi-axis. Some optimization of the crystal size was required since the optical penetration depth was rather low. A crystal of dimensions each < 50 μm appeared to be necessary in order that the crystal did not break up upon laser excitation. Circular polarization was used in order to preclude any preferential directional effect of optical absorption and successful laser excitation was achieved using the eighth chosen crystal ($50 \times 40 \times 40$ μm).

Before laser excitation, a data collection was undertaken in order to obtain a reference ground-state structure of the material. Data were collected over a phi range of 360° , in 2° steps, each step having a 1° overlay from the last point, thus enabling an inherent two-fold statistical averaging of each frame. The four-fold rotational redundancy also aided significantly the statistical quality of data. Data were collected using a MAR-CCD detector.

The crystal was then laser excited and two sets of data were collected, using the same data collection strategy as above. In the first of these data collections, a -10ns time delay between the laser and X-ray pulses was imposed so that they would purposely not be synchronized, and data would only be collected when the excited-state of the crystal had relaxed. This enabled a data collection of the ground state structure but encompassing any effects of laser heating. The laser and X-rays were then synchronized and an excited-state data collection was undertaken. The difference between these two data collections should provide an excited-state structure that precludes any artefacts from any laser-induced effects.

All data have been indexed and are presently being processed using MOSFLM software - default features have been adapted to optimize processing for small-molecule diffraction rather than protein crystallography for which the program is nominally intended. An empirical absorption correction routine is also being developed in order to correct for absorption very accurately, since the suspected area of charge-transfer owing to the excited-state is close to the rhenium atom, where absorption will be at its largest.

After a first attempt at processing, the data consistency looks good and the internal statistical agreement ranges from 0.05-0.10, which is good for this detection methodology. In each case, about 3700 unique reflections are observed with about 32-fold redundancy. Refinement appears to indicate that the lateral positioning of the phi-axis with respect to the detector was not quite parallel, but a geometrical correction will be possible to overcome this problem.

Data processing is continuing along with the optimization of processing methodology itself. This experiment therefore represents a first key feasibility experiment with the oscillatory method of nanosecond time-resolved single-crystal diffraction of photo-induced species.