（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。）

MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2014A0027 実験課題名 Title of experiment Neutron Diffraction Study of Metal Complex Using Porous Coordination Complexes as Crystalline Hosts 実験責任者名 Name of principal investigator Yasuhide Inokuma 所属 Affiliation Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo	装置責任者 Name of responsible person Takashi Ohhara 装置名 Name of Instrument/（BL No.） BL-18 実施日 Date of Experiment 2014/11/15~2014/11/25

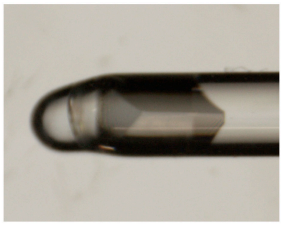
試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Guest included porous coordination crystal

$(C_6H_5)_3GeH \subset [(TPT)_2(ZnI_2)_3]_n$ TPT(tri(4-pyridyl)1,3,5-triazine)

Size: 2.0 × 1.0 × 0.3 mm^3



2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

This experiment is aimed to show the applicability of recently developed new technique called ‘Crystalline Sponge Method’ for neutron diffraction analysis of non-crystalline organometallic hydride compounds. A porous coordination network crystal $[(TPT)_2(ZnI_2)_3]_n$ is used as a crystalline sponge that absorb organometallic compounds from a contacting solution to align them in the crystal pores so that they can be analyzed by X-ray diffraction analysis. Although the method was so far limited to single crystal X-ray analysis because of the host crystal size, this time we succeeded to synthesize millimeter–sized crystals that would match the requirement of neutron diffraction analysis. Metal hydride complexes are of interesting because of their reactivity and catalytic activities. One of the most important data of metal hydride complexes is the position (i.e. H-M bond length) of the hydride. X-ray diffraction analysis, however, cannot precisely determine the positions of hydride ligands. Given general interest of metal hydride complexes, we designed the project of neutron diffraction analysis of them using big size crystalline sponges.

2. 実験方法及び結果（つづき）Experimental method and results (continued)

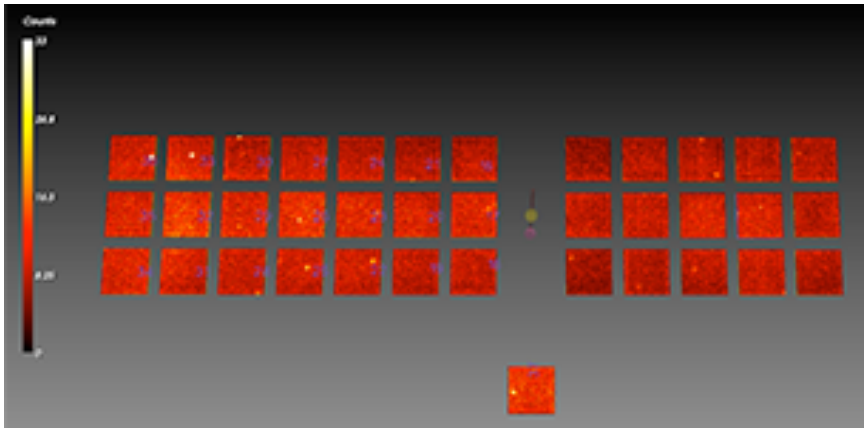


Fig. 1. A diffraction image of $Ph_3GeH@[(TPT)_2(ZnI_2)_3]_n$.

The sample crystal was prepared by soaking method. A crystal of $[(TPT)_2(ZnI_2)_3]_n$ was placed in a quartz capillary with a cyclohexane/nitrobenzene solution of triphenyl germanium hydride at room temperature over 15 days. The end of the capillary was sealed with wax and subjected to neutron diffraction analysis using SENJU at BL-18 in MLF over 8 days at 40 K. The data analysis was carried out with 10887 reflections up to 1.0 Å resolution using STARGazer program. (Fig. 1) The lattice parameters were determined to be monoclinic *C*2/*c* *a*=35.376(4), *b*=15.0635(10), *c*= 30.459(5), β=102.605(10)°. Using the coordinates of non-hydrogen atoms obtained from single crystal X-ray data, the neutron diffraction data was refined and hydrogen atoms were generated. We could see the nuclear densities for hydrogen atoms with the R_1 value of 0.3111 for 1211 observed reflections ($|F_o| > 2\sigma(F_o)$). (Fig. 2) The bond distance between Ge-H was thus estimated to be 1.6 Å.

Since the measurement temperature of neutron diffraction was 40 K which is different from that of X-ray analysis (90 K), it is necessary to re-measure the X-ray data at the same temperature to publish the result. We are now negotiating with a collaborator of Spring-8 about the possibility of low-temperature measurement of X-ray data.

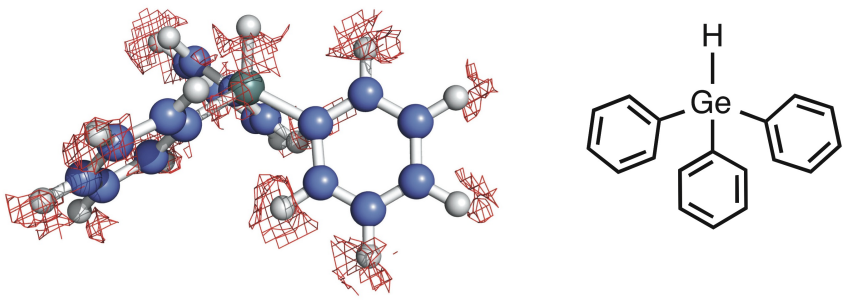


Fig. 2. Nuclear density map (contour at σ = -1.0) of crystal $Ph_3GeH@[(TPT)_2(ZnI_2)_3]_n$.