Experimental report

23/01/2019

Proposal:	**5-23-700**	**Council:**	4/2017
Title:	Diffusion pathways determination of new Mo6 cluster-based protonic conductors by high-resolution neutronpowder diffraction		
Research area:	Materials		

This proposal is a new proposal

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Samples: $(D_2)[Mo_6X_8(OD)_6].12D_2O$ (X = Cl, Br)
$(D_4)[Mo_6Br_6S_2(OD)_6].12D_2O$
$(H_2)[Mo_6X_8(OH)_6].12H_2O$ (X = Cl, Br)
$(H_4)[Mo_6Br_6S_2(OH)_6].12H_2O$

Instrument	Requested days	Allocated days	From	To
D2B	3	3	06/04/2018	09/04/2018

Abstract:

Inorganic Mo6 cluster compounds exhibit a wide range of physical properties such as superconductivity, magnetism, luminescence, thermoelectricity, and ionic mobility. Recently, electrochemical impedance spectroscopy results highlight hydrogen mobility in both $(H)_2[Mo_6X_8(OH)_6].12H_2O$ (X = Cl, Br) and the new cluster compound $(H)_4[Mo_6Br_6S_2(OH)_6].12H_2O$, supported by ab initio molecular dynamics simulations. The analogous deuterium compounds are also synthesized. Unfortunately, the determination of the diffusion pathways of hydrogen/deuterium atoms in these new protonic conductors using the bond-valence sum method cannot be done without an exact knowledge of the crystal structure of these materials, especially atomic positions, site occupancies and displacement parameters of hydrogen/deuterium atoms. For these reasons, high resolution neutron powder diffraction data are needed to determine accurately the crystal structure in order to analyze the hydrogen/deuterium diffusion pathways. This work is part of the Ph.D. of Gilles

Experimental report on the proposal 5-23-700: *Diffusion pathways determination of new Mo_6 cluster-based protonic conductors by high-resolution neutron powder diffraction.*

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1. Introduction

Inorganic octahedral Mo_6 cluster compounds exhibit a wide range of physical properties such as superconductivity [1-3], magnetism [2,4], luminescence [5-7], thermoelectricity [8-11], and ionic mobility [12-17]. Recently, electrochemical impedance spectroscopy results highlighted hydrogen mobility in both $(H)_2[Mo_6X_8(OH)_6]\cdot 12H_2O$ (X = Cl, Br) and the new cluster compound $(H)_4[Mo_6Br_6S_2(OH)_6]\cdot 12H_2O$, supported by *ab initio* molecular dynamics simulations [18]. Unfortunately, the determination of the diffusion pathways of hydrogen atoms in this new class of multifunctional luminescent – proton-conducting materials cannot be done without an exact knowledge of the crystal structure of these materials, especially atomic positions, site occupancies and displacement parameters of hydrogen atoms. For these reasons, high-resolution neutron powder diffraction data were recorded on D2B in order to determine accurately the crystal structure, and then, to analyze the hydrogen/deuterium diffusion pathways.

2. Crystal structure determination of $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$

The crystal structure of the $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$ compound ($R\bar{3}m$, *a* = 15.125(1)Å, *c* = 10.960(1) Å), and in particular the localization of hydrogen atoms, was successfully determined from high resolution neutron powder diffraction (NPD) data recorded at 20 K (Figure 1). Presence of ice in its hexagonal structure ($P6_3mmc$, *a* = 4.495(1) Å, *c* = 7.319(1) Å), arising from solvent, was also detected in the sample and considered in the refinement.

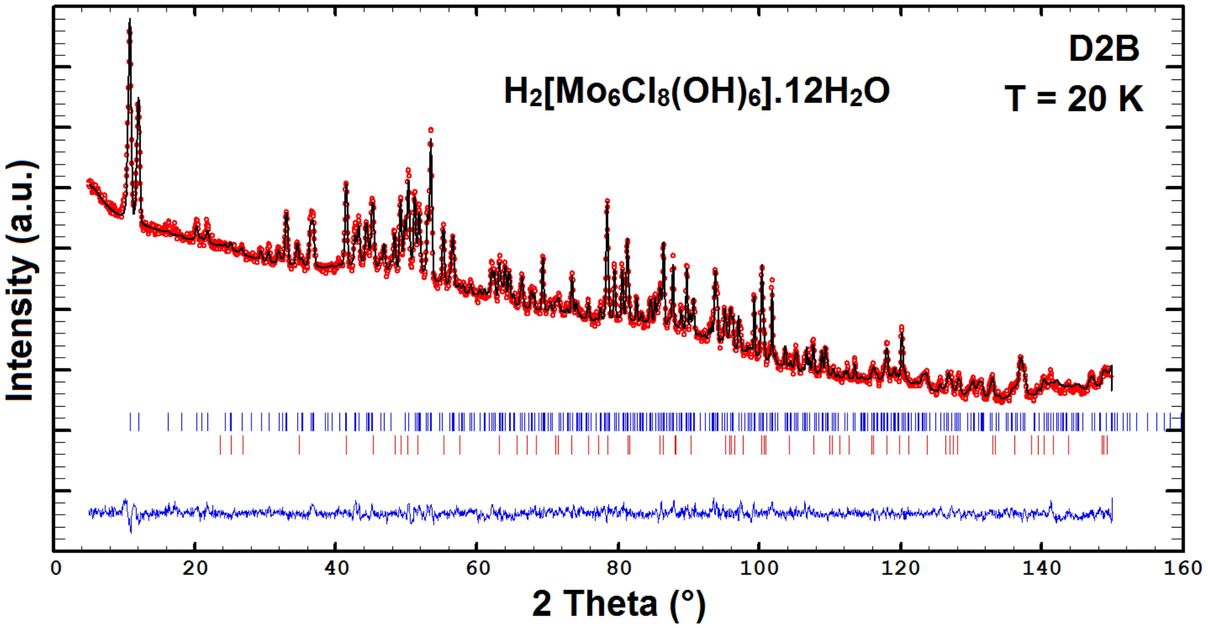

Figure 1: Rietveld refinement against neutron powder diffraction data of $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$ recorded at 20 K (λ = 1.594 Å, D2B): R_{wp} = 0.979, R_{Bragg} = 11.3 Chi^2 = 1.76. Second sets of diffraction peaks are related to ice arising from the aqueous solution.

The crystal structure of $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$, built from $[Mo_6Cl_8]$ cluster cores with oxygen atoms on apical positions as well as arising from crystallization water molecules (Figure 2) [18], was confirmed by NPD data. Localization of hydrogen atoms was determined by Fourier maps using the GFourier program implemented in the FullProf Suite [19] and crystal chemistry considerations.

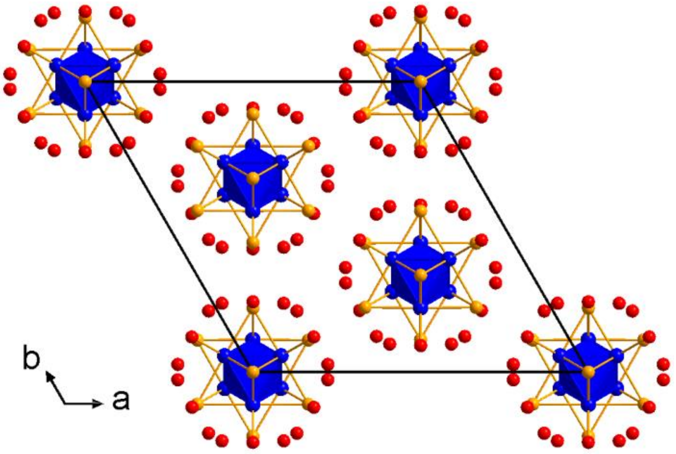

Figure 2: Crystal structure representation of the cluster units and of oxygen atoms arising from the crystallization water molecules in $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$.

The results indicate that (i) H1 atoms are located between two oxygen atoms in apical position (named O1 in Figure 3) at a distance of 1.285 Å, (ii) H2 and H3 atoms, each on a crystallographic site of general multiplicity with a site occupation factor of 0.5, are linked to oxygen atom arising from the crystallization water molecules (named O2 in Figure 3) at interatomic distances of 1.025 Å and 0.975 Å, respectively, (iii) H4 atoms are located between O1 and O2 at distances of 1.528 Å and 1.228 Å, respectively, and (iv) H5 atoms are between two O2 atoms at a distance of 1.369 Å. From this crystal structure description, it should be noted that H1, H4 and H5 atoms are shared between two oxygen atoms, leading to O-H distances longer than that expected (Figure 3). Moreover, these atoms are characterized by higher isotropic displacement parameters than those refined for H2 and H3 atoms. These structural features suggest that the protonic mobility of this material is mainly related to the H1, H4 and H5 atoms.

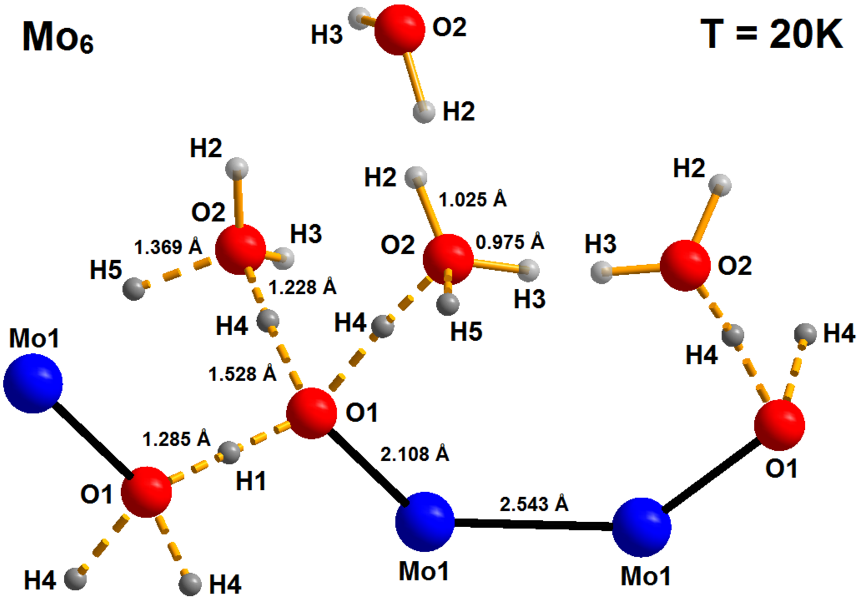

Figure 3: H-bonds network in $H_2[Mo_6Cl_8(OH)_6]\cdot 12H_2O$ at 20 K

In order to confirm this structural-properties relationship and to determine accurately the hydrogen diffusion pathways in this protonic conductor material [18], both Rietveld refinements performed on high resolution NPD data recorded at 200 K and 300 K as well as maximum entropy method (MEM) analyses are in progress. These results, that will be completed by *ab initio* molecular dynamics simulations, will allow to further advance knowledges on this new class of protonic conductors and will be the subject of a future scientific publication.

3. References

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