Experimental report

01/11/2022

Proposal: **5-21-1174** **Council:** 4/2021

Title: Crystal structure and magnetism ofthe iridium(IV) complex compounds Na2IrCl6 and Na2IrCl6*6D2O

Research area: Chemistry

This proposal is a new proposal

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Samples: Na2IrCl6*6D2O

Instrument	Requested days	Allocated days	From	To
D1B	1	1	30/08/2021	31/08/2021

Abstract:

M2[IrCl6] (M = Li, Na, K, Rb, Cs, NH4) and their hydrates have raised interest recently as spin-orbital-induced semiconductors with hydration-dependent structural and magnetic variations. Na2IrCl6*6H2O is a red-brown solid and is paramagnetic down to 2 K. The crystal structure is known except for hydrogen positions. The water-free Na2IrCl6 is described as canted antiferromagnet (weak ferromagnet) at low temperatures (TN = 2.7 K), but may also be ferrimagnetic. Neutron diffraction is well-suited to distinguish between the two alternative explanations. The aim of this study is to determine deuterium positions in Na2IrCl6*6D2O, follow the formation of Na2IrCl6 by D2O loss upon heating and the development of magnetic ordering upon cooling Na2IrCl6 to 2 K.

Crystal structure and magnetism of the iridium(IV) complex compounds Na_2IrCl_6 and $Na_2IrCl_6*6D_2O$ (experiment 5-21-1174)

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Objectives

The aim of this study was to determine deuterium positions in $Na_2IrCl_6*6D_2O$, to follow the formation of Na_2IrCl_6 by D_2O loss upon heating and the evolvement of magnetic ordering upon cooling of Na_2IrCl_6 to 2 K. This study was meant to be a contribution to the relatively unexplored magnetochemistry of iridium(IV) coordination compounds. Therefore, we have taken temperature dependent neutron powder diffraction data on a $Na_2IrCl_6*6D_2O$ sample on D1B.

Experimental Details

$Na_2IrCl_6*6D_2O$ was synthesized as a brown powder by methods known from literature [1] and characterized by X-ray powder diffraction and infrared spectroscopy. Neutron diffraction patterns were collected as a function of temperature in a cryofurnace ($2\ K \leq T \leq 400\ K$) on the neutron powder diffractometer D1B with data collection times of 300 s per pattern (Figs. 1 and 2). The sample was enclosed in a vanadium container of 5 mm outer diameter with some stone wool on top, a copper seal with two holes to allow for gas exchange and a loosely closed lid. These measures were meant to allow for D_2O to leave the sample container upon heating without blowing out the powder into the cryofurnace. The following temperature protocol was followed: measurement at room temperature (NUMORS 544827–42), applying vacuum and then heating with 100 s/K to 400 K (NUMORS 544844–82), hold for 600 s (NUMORS 544883–86, 15 min runs), cooling to 20 K with 30 s/K and to 2 K with 200 s/K (NUMORS 544887–941), and finally holding at 2 K (NUMORS 544942–969).

Results and Discussion

The neutron powder diffraction pattern at room temperature did not correspond to $Na_2IrCl_6*6D_2O$ as expected from the laboratory based characterization, but to a mixture of hydrated phases, probably with partial H/D exchange and at least one unknown phase. Probably, the sample had partially decomposed although it was considered to be stable from earlier investigations. From these patterns it was not possible to determine hydrogen (deuterium) positions in $Na_2IrCl_6*6D_2O$, as initially planned. During heating the background dropped in two steps, one around 310 K, the second around 340 K (Fig. 1). In the first step, the higher hydrates decomposed to the dihydrate, which reduced the amount in incoherent scattering accordingly. The second step of background reduction most probably corresponds to driving out water from the sample completely, which according to literature [1] and earlier lab-based studies should result in water-free monoclinic Na_2IrCl_6. At present, the product of the thermal decomposition of $Na_2IrCl_6 * 6D_2O$ (Fig. 1) remains unclear. Water-free Na_2IrCl_6 in the expected crystal structure [1] can be excluded. Upon cooling, no phase transition occurs, neither structural nor magnetic (Fig. 2). Without identification of the product, no meaningful data analysis can be performed. We have been trying to reproduce the results by laboratory based X-ray powder diffraction, in order to characterize and identify the decomposition product. So far, however, we were not able to reproduce the findings from the neutron diffraction experiment. Therefore, we tentatively conclude that $Na_2IrCl_6 * 6D_2O$ did not decompose as expected, but some other reaction has taken place, e. g. hydrolysis with the water freed by decomposition. Another option might be the production of another polymorph of Na_2IrCl_6, however, any indexing attempt of the powder pattern did not succeed as yet.

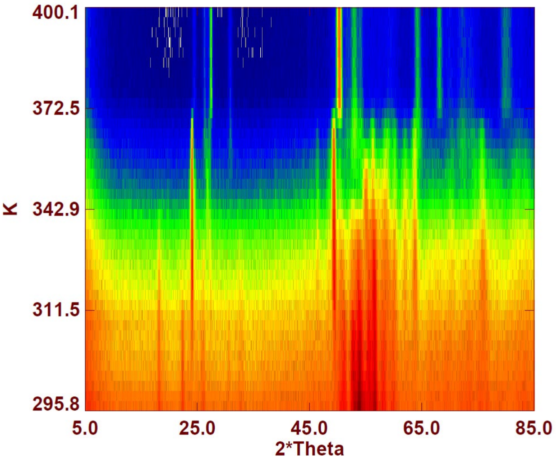

Fig. 1: Neutron powder diffraction patterns of $Na_2IrCl_6 * 6D_2O$ while heating under vacuum (D1B, $\lambda = 2.52$ Å)

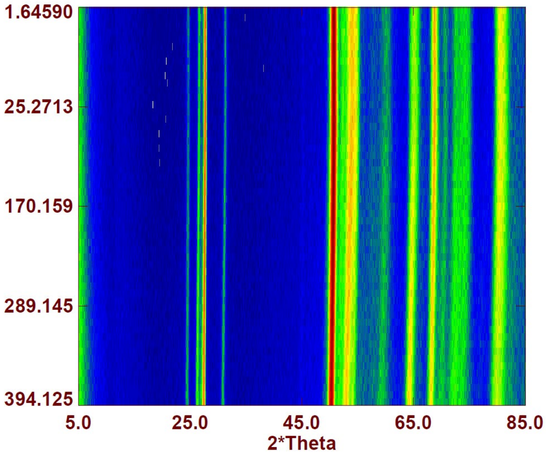

Fig. 2: Neutron powder diffraction patterns of the reaction product (see Fig. 1) while cooling (D1B, $\lambda = 2.52$ Å)

Literature

[1] S. [1] S.-S. Bao, D. Wang, X.-D. Huang, M. Etter, Z.-S. Cai, X. Wan, R. E. Dinnebier, L.-M. Zheng, *Inorg. Chem.* **2018**, *57*, 13252−13258