Poster

Crystallographic study of $NaClO_3$ and $NaBrO_3$: addressing misconceptions about chirality, absolute configuration, and optical rotation

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The achiral ionic salts, $NaClO_3$ and $NaBrO_3$, readily form large, chiral cubic crystals from aqueous solution in the space group $P2_13$. Isomorphous crystals of these salts which have the same absolute configuration rotate polarised light in opposite directions. For most undergraduate students, this is counterintuitive. Generally, the only exposure undergraduate students have to chirality is in organic (and sometimes coordination) chemistry. What is often overlooked is the fact that chirality, and specifically absolute configuration, is not related to the rotation of polarised light. It is also not appreciated that achiral molecules or ions can pack together to form chiral crystals.

There is a vast amount of literature on $NaClO_3$ and $NaBrO_3$ (dating from the first crystal structure reported in 1921 [1] to 2024 [2]). Seminal papers on crystals of $NaClO_3$ include observations by Kondepudi on the effect of stirring on crystallisation, usually resulting in only one chiral form of $NaClO_3$ [3]; by Viedma, on the use of grinding to purify a mixture of *d*- and *l*-$NaClO_3$ [4]; and by Soai, on the autocatalysis of chiral molecules from achiral precursors, using chiraly pure $NaClO_3$ [5]. There is therefore an enormous scope for a 10-week BSc Honours research project [6].

In this paper we discuss several results of the research project, focusing on the experimental determinations of the absolute chirality of $NaClO_3$ and $NaBrO_3$ crystals. Large crystals of $NaClO_3$ were inspected under a polarising microscope to determine the optical rotation of polarised light. The absolute configuration of a $NaClO_3$ crystal, which rotated polarised light to the left (+), was determined by means of single-crystal X-ray diffraction methods. The data collection of a full sphere of reflections took 10 minutes. The same $NaClO_3$ crystal was used to seed an aqueous solution of $NaBrO_3$, which then yielded isomorphous crystals of $NaBrO_3$. The absolute configuration of one of these $NaBrO_3$ crystals was again determined using single-crystal X-ray diffraction. The crystals were labelled *l*-$NaClO_3$ and *d*-$NaBrO_3$, where *l*- and *d*- refer to opposite absolute configurations. As reported in literature, the rotation of polarised light for these crystals of opposite chirality was, counterintuitively, in the same direction: *l*-(+) $NaClO_3$ and *d*-(+) $NaBrO_3$.

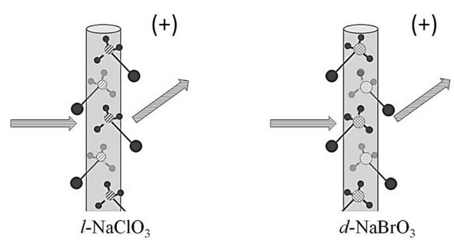

Figure 1. *l*-$NaClO_3$ (left) and *d*-$NaBrO_3$ (right) rotate polarised light in the same direction (adapted diagram from the PhD of Manon Schindler, with permission)

[1] Dickinson, R. G., & Goodhue, E. A. (1921). *J. Am. Chem. Soc*, **43(9**), 2045.

[2] Zhang, B., Coquerel, G., Park, B. J., & Kim, W. S. (2024). *Cryst. Growth Des.* **24(3)** 1042.

[3] Kondepudi, D. K., Kaufman, R. J., & Singh, N. (1990). *Science*, **250**, 975.

[4] Viedma, C. (2007). *Cryst. Growth Des*, **7(3)**, 553.

[5] Sato, I., Kadowaki, K., & Soai, K. (2000). *Angew. Chem. Int. Ed.,* **112(8)**, 1570.

[6] At the University of the Witwatersrand, Johannesburg, South Africa, students complete a three-year BSc, followed by a one- year Honours degree, which includes two short research projects.