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Editorial

Chemistry for Space Group Symmetry beyond Crystals

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As a recent cutting-edge research target, the prediction of crystal systems or space groups using machine learning based on databases has been actively reported [1–4]. Typically, algorithms for the prediction of space groups from chemical composition are developed mathematically [1]. Their predominant purpose may be using in powder X-ray diffraction (XRD) analysis [2]; therefore, their applications for inorganic solid compounds have been frequently reported so far [3,4].

Space group statistics have been investigated for many years alongside the development of the amount of recorded data in databases on crystal structures. As for inorganic crystals, research has been progressing for a long time, and our understanding is deepening. In 1967, Nowacki et al. [5] reported the statistics of the frequency of the then-known space groups of inorganic and organic crystals. One of the authors also explained the research regarding oxides and hydroxides (inorganic crystals) in his native language, and a mathematician (Itoh) from the same country mathematically discussed statistical distributions with simulation calculations using Poisson distribution models [6]. In 2009, Urusov et al. [7] reported the frequency distribution of space groups for inorganic compounds. According to their theory, which focuses on the Wyckoff position, they reported that the space groups of inorganic crystals are holohedral and centrosymmetric, with many of the 24 specific types, and that there are rare space groups and space groups that have never been seen before.

The databases recorded for organic compounds and organometallic compounds, such as the Cambridge Structural Database (CSD) [8], are different from those for inorganic compounds. In 1983, Mighell et al. [9] reported space group frequency for organic compounds, in which they mentioned that there were no examples of 35 space groups. With the technology available at the time, there were reports of incorrect space groups, and the reasons for this were also considered. Srinivasan [10] mentioned chirality and space group frequency as properties unique to organic compounds in 1992. Mirror symmetry between enantiomeric space groups seems to be the motivation for this study. Subsequently, in 2020, Rekis et al. [11] reported on extraction and statistics using the CSD Python API for database use regarding chiral compounds. They discuss crystallization, diastereomers, chiral crystals of achiral compounds, etc., which are also related to classical natural crystallization. Focusing on conformational changes and polymorphisms of organic compounds (of pharmaceutical importance), Singh et al. [12] reported in 2017 on space group frequency as information necessary for crystal structure prediction.

On the other hand, protein crystallography (included in the Protein Data bank (PDB)) is a category that inherently has chirality due to L-amino acids. Gaur et al. [13] reported space group frequencies for soluble and membrane proteins in 2021. Brink [14] raised the issue of bridging databases between chemical crystallography (CSD) and protein crystallography (PDB).

Chiral crystallization of small molecules of organic compounds must be an exceptional phenomenon of molecular symmetry and space groups; it was summarized by Putman in 2022 [15]. Of course, in addition to typical examples of quartz (SiO_2), achiral inorganic

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compounds can crystallize in chiral space groups with helical alignment. Fecher et al. [16] closely investigated achiral and chiral space groups and chiral crystal structures for inorganic solids. Intentionally, achiral organic compounds can be designed to form chiral crystals attributed to supramolecular assemblies of helical structures [17].

Salen-type Ni(II) complexes are known to form dimers. If there is an asymmetric carbon between two nitrogen atoms, there can be a chiral/achiral molecule. Dimers of enantiomers may be related by centers of symmetry, disorder around asymmetric carbons (where one substituent is hydrogen) may be possible, and space group asymmetry may be less likely to be reflected. This makes indexing difficult in powder analysis (even if the single crystal structure of a complex prepared from racemic amine and its $P2_1/c$ space group are known), as shown in Figure 1. Are data and theory effective in determining space groups in the early stages of analysis?

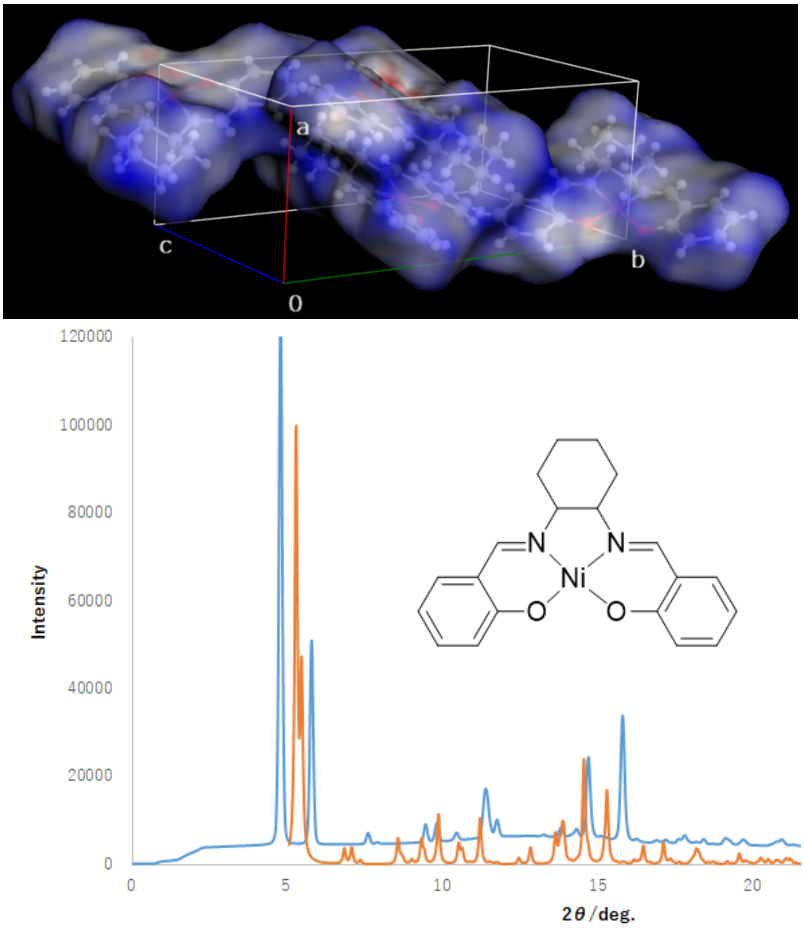

Figure 1. (**Above**) Hirshfeld surface of unit cell of a salen-type Ni(II) complex (CCDC 722,825) [18]. (**Below**) Simulated (orange) and experimental (blue) powder XRD patterns of the nickel(II) complex.

Beyond crystals, the symmetry of molecules and molecular assemblies will influence the symmetry of supramolecular aggregations. As a future concept, an aggregate of chiral salen-type Gd(III)-Ni(II) complex cations of the *P*1 space group [19] and chiral azobenzene derivative Cu(II) complex anions will be dispersed in a Poly(methyl 2-methylpropenoate) (PMMA) polymer film to induce anisotropic orientation due to the Weigert effect. In future, we would like to observe reliable "spatial" information on supramolecular orientation or the alignment of such hybrid materials induced by polarized ultraviolet light (Figure 2). Will theories and data utilization methods that can handle everything from the symmetry of molecules to the symmetry of molecular assemblies be developed in the future?

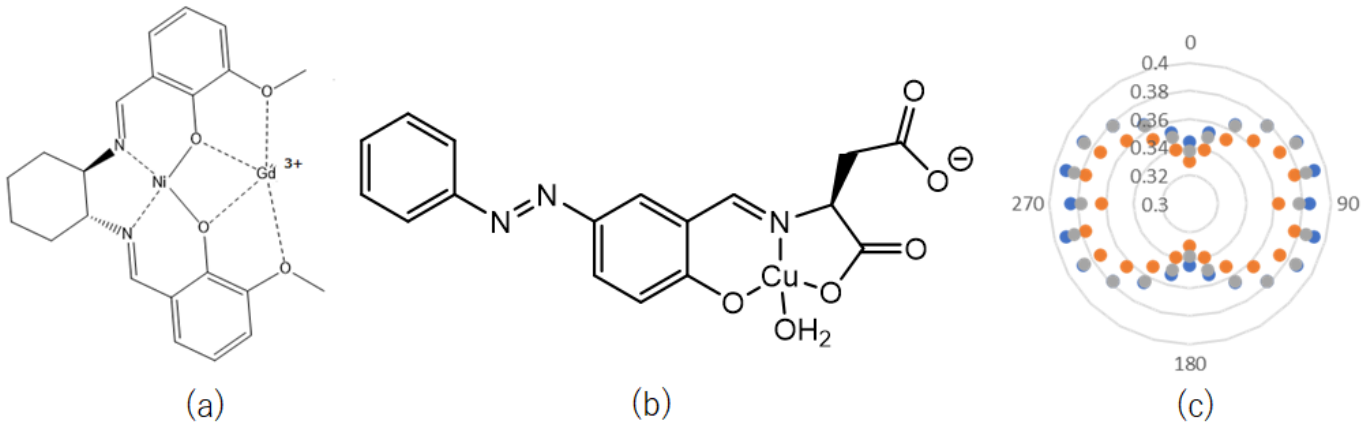

Figure 2. (**a**) Chiral Gd(III)-Ni(II) complex cation [19], (**b**) chiral azo Cu(II) complex anion, and (**c**) preliminary circular plots of intensity at 403 nm due to Gd(III)-Ni(II) complex (indicating anisotropic orientation) before (blue) and after UV (orange) and visible (gray) polarized light irradiation.

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