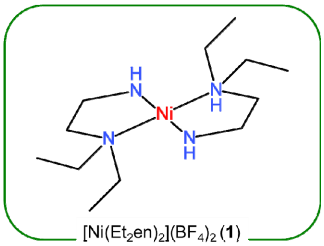
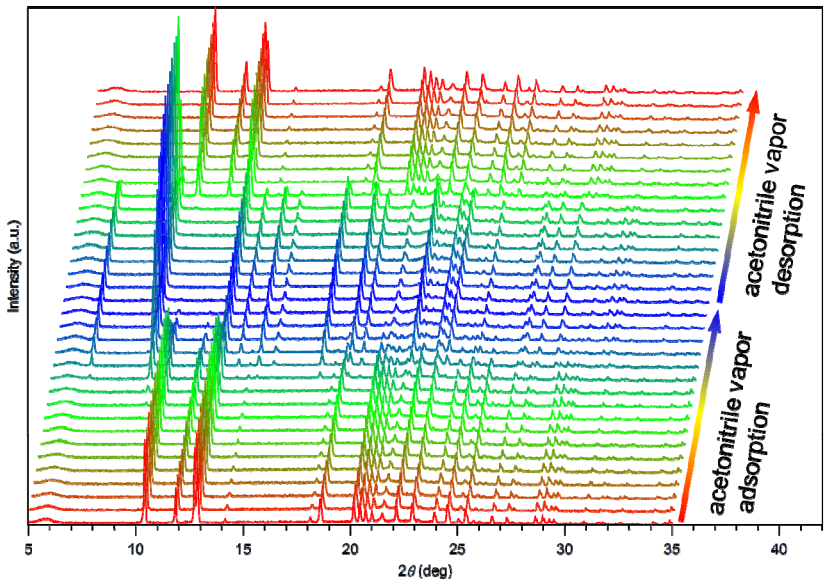
Application of Integrated X-ray Powder Diffraction Software: PDXL

Ni(II)-N,N-Diethylethylenediamine Complex

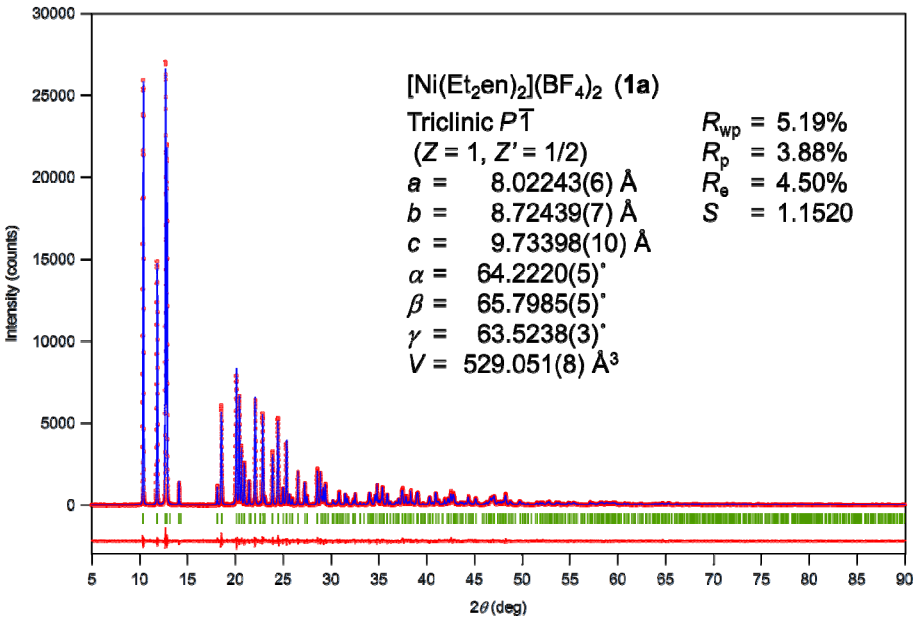


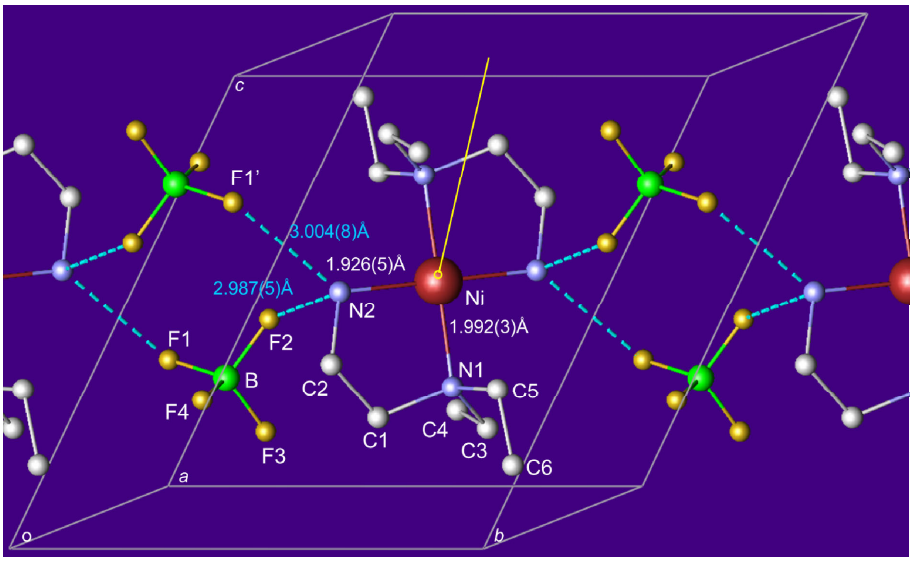
One of the Ni(II) complexes, $[Ni(Et_2en)_2](BF_4)_2$ (**1**), is known to show thermochromism. The complex **1** turns from orange to red abruptly at around 100ºC. The crystal structures of both low-temperature phase (**1a**) and high-temperature phase (**1b**) have been determined from their powder diffraction data.

We also examined the structural change of complex **1**, which was induced by solvent vapor. **1** did not show hydration and dehydration transition along the change in vapor pressure of water, however, **1a** powder turned to light blue under acetonitrile vapor.

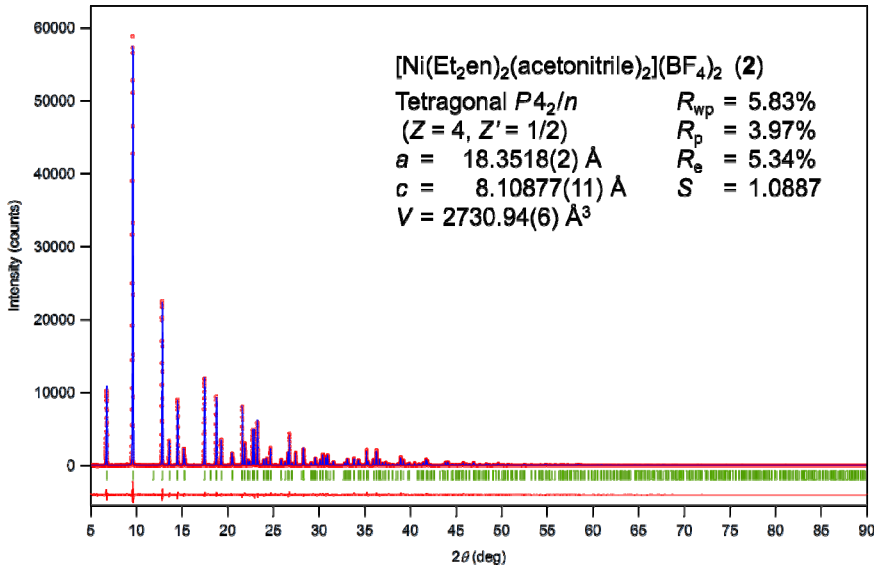


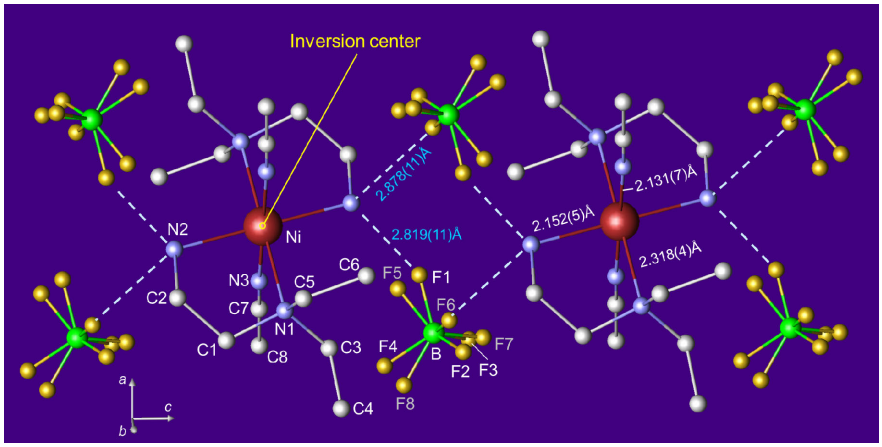
Powder diffraction patterns were measured by changing the vapor concentration of acetonitrile. The diffraction pattern of **1a** turned to that of **2** when the acetonitrile vapor concentration increased. When decreasing the vapor concentration, the diffraction pattern reverted to that of **1a**. Neither amorphous nor crystalline phases other than **1a** and **2** were observed, which indicates the transitions **1a** to **2** and **2** to **1a** occurred crystal-to-crystal.





In the crystal structure of **1a**, the Ni atom is located on the inversion center, and two Et_2en molecules are chelating to the Ni atom and form a square planar structure. $[Ni(Et_2en)_2]^{2+}$ connects to two tetrafluoroborate anions, and they form a 1-D chain structure through hydrogen bonds along the *b* axis.





The crystal structure of the complex **2** was determined using powder diffraction technique also. The initial structure of **2** using direct-space methods was succeeded by assuming Ni atom is located on the inversion center. The chemical composition of **2** is $[Ni(Et_2en)_2(acetonitrile)_2](BF_4)_2$, and **2** forms octahedral structure where two acetonitrile molecules coordinate to the Ni atom of the square planar $[Ni(Et_2en)_2]^{2+}$ from the axial direction. As shown here, tetrafluoroborate anion structure was analyzed as a disordered or a thermal-vibration model, and the measured data and calculated data were in good agreement with each other.

Molecules **2** are connected by two molecules of tetrafluoroborate through hydrogen bonds, which is similar to the **1a** structure, and form a 1-D chain structure along the *c* axis. No strong interactions between the 1-D chains are observed, though.

Thus, the transition behavior was clarified based on the differences in crystal structures of the complexes.