

# Investigation of anomalous compressibility and thermal expansion of a copper(II) coordination polymer

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The coordination polymer catena-poly[[{4-bromo-2-[2-(dimethyl-amino)ethyliminomethyl]phenolato}-copper(II)]- $\mu$ -thiocyanate] (C<sub>12</sub>H<sub>14</sub>N<sub>3</sub>OSBrCu) is a compound exhibiting weak magnetic properties under ambient conditions. Its characteristic “zig-zag” arrangement of Cu<sup>2+</sup> cations linked by SCN<sup>-</sup> anions makes it a potential candidate for compressibility studies [1]. We therefore decided to investigate the structural response of this material to temperature and pressure in order to determine whether it displays anomalous compressibility or unusual thermal expansion.

Single-crystal X-ray diffraction experiments were performed at ambient pressure between 120 K and 320 K, and at room temperature at pressures up to 8.3 GPa, utilizing a diamond anvil cell and in-house X-ray source as well as synchrotron facility. To address the challenge of low data completeness under high pressure, an optimized crystal orientation protocol [2] was implemented, resulting in high quality data with coverage of 86 % up to 0.83 Å resolution.

Similarly to formerly studied simpler Cu(II) coordination polymers [1], temperature dependent experiments revealed no unusual thermal expansion behavior over the studied range, indicating the absence of phase transitions or *anomalous* volume changes.

In pressure-dependent experimental series, the influence of pressure medium on the sequence of structural transformations was observed. In a non-hydrostatic medium (Paraton oil), the polymer passed through a series of symmetry-lowering phase transitions; in a quasi-hydrostatic medium (1:1 n-pentane/isopentane mixture), no phase transitions occurred. A Cu...Cu distance shortening indicative of stronger magnetic effects has been observed at the highest investigated pressure.

[1] Cliffe, M. J.; Lee, J.; Paddison, J. A. M.; Schott, S.; Mukherjee, P.; Gaultois, M. W.; Manuel, P.; Siringhaus, H.; Dutton, S. E.; Grey, C. P. *Phys. Rev. B* **2018**, 97 (14), 144421. <https://doi.org/10.1103/PhysRevB.97.144421>.

[2] Tchoń, D.; Makal, A. *IUCrJ* 2021, 8, 1006–1017.

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