

โครงสร้างโมดูลเลตได้สัดส่วนสัมพันธ์กันของคอปเปอร์ไบไพริดีนซัลเฟตโคออร์ดิเนชันพอลิเมอร์โคริสตัลไลซ์กับกรดทerephthalic

## THE COMMENSURATELY MODULATED STRUCTURE OF COPPER (4,4'-BIPYRIDYL) SULFATE COORDINATION POLYMER COCRYSTALLIZED WITH TEREPHTHALIC ACID

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**บทคัดย่อ :** โคริสตัลไลน์พอลิเมอร์คอปเปอร์ไบไพริดีนซัลเฟตโคออร์ดิเนชันพอลิเมอร์โคริสตัลไลซ์กับกรดทerephthalic ถูกสังเคราะห์โดยวิธีปฏิบัติกรรมกิจความร้อน ในหนึ่งหน่วยของโมดูลเลตประกอบด้วย 2 หน่วยสูตรของคอปเปอร์ไบไพริดีนซัลเฟตกับกรดทerephthalic โครงสร้างถูกอธิบายได้โดยโมดูลเลชันได้สัดส่วนสัมพันธ์กันของคอปเปอร์ไบไพริดีนซัลเฟตกับกรดทerephthalic ซึ่งในโมดูลเลตเกิดสายโพลิเมอร์ของคอปเปอร์ไบไพริดีนซัลเฟตและลิแกนด์ไบไพริดีนแพรโดย  $n$  glide อีออนซัลเฟตอยู่บนแกน 2-fold เชื่อมต่อ คอปเปอร์-ออกซิเจน-ซัลเฟต-ออกซิเจน-คอปเปอร์สายโพลิเมอร์เข้าไปในโคริสตัลไลน์พอลิเมอร์ริบบิ้นสายคู่ ริบบิ้นสายคู่เชื่อมระหว่างกันโดยกรดทerephthalic บนจุดศูนย์กลางของลิแกนด์ นั่นคือ พันธะไฮโดรเจนไปยังอะตอมออกซิเจนอิสระของการเชื่อมลิแกนด์เชื่อมซัลเฟตให้ปรากฏขึ้นไปยังโครงสร้างพหุสามมิติ

**Abstract:** The coordination polymer *Cu*-(4,4'-bipyridyl)sulfate cocrystallized with terephthalic acid was synthesized by thermal reaction. The asymmetric unit contains two formula units of  $[\text{Cu}(4,4'\text{-bipy})]_2(\text{SO}_4)_2\text{HO}_2\text{C-C}_6\text{H}_4\text{-CO}_2\text{H}$ . The structure is described as a commensurate modulation of an idealized  $Z = 2$  parent structure. In the parent, polymeric chains of alternating copper atoms and 4,4'-bipyridine ligands  $[-\text{Cu}'\text{-bipy-Cu}'\text{-bipy-}]$  are propagated by an  $n$  glide. Sulfate ions on 2-fold axes bridge  $[-\text{Cu-O-S-O-Cu-}]$  the polymeric chains into a double ribbon coordination polymer. The double ribbons are interconnected by terephthalic acids on inversion centers hydrogen bonded to free oxygen atoms of the bridging sulfate ions giving rise to a 3-dimensional network structure.

**Experimental:** Solvothermal reaction of the copper sulfate, terephthalic acid, and 4,4'-bipyridine gave rhombic slabs of a yellow product with composition  $[\text{Cu}(4,4'\text{-bipy})]_2(\text{SO}_4)_2\text{HO}_2\text{C-C}_6\text{H}_4\text{-CO}_2\text{H}$ . Data were collected at 295 K on a SMART CCD diffractometer equipped with a molybdenum x-ray source. Structure refinement with RAELS (1)

*Crystal data:*  $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)]_2(\text{SO}_4)_2 \cdot 2(\text{C}_8\text{H}_6\text{O}_4)$ ; monoclinic;  $(2, c) \cdot a = 19.597(4)$  Å,  $b = 34.771(2)$  Å,  $c = 16.274(3)$  Å,  $\beta = 107.52(3)^\circ$ ,  $V = 10,574.8$  Å<sup>3</sup>;  $Z = 8$ ;  $D_m = 1.765$  Mg m<sup>-3</sup>,  $\lambda_{\text{MoK}\alpha} = 0.71073$  Å; data collected, total 86,910 (including  $C$  absences), unique 11,991 (excluding  $C$  absences),  $R_w = 0.0526$ , 5023 observed  $(I > 3\sigma(I))$ .

**Results, Discussion, and Conclusion:** The structure can be understood as a commensurate displacive modulation of an idealized  $Z = 2$  parent structure with  $a_p = a/2$ ,  $b_p = b/2$ ,  $c_p = c$ . In the parent, polymeric  $[-\text{Cu}'\text{-bipy-Cu}'\text{-bipy-}]$  chains are propagated by an  $n$  glide,  $1/2+x$ ,  $1/2-y$ ,  $1/2-z$ , and are cross linked (Cu-O-S-O-Cu) by the sulfate groups which lie on 2-fold axes. The terephthalic acids are on centers of inversion hydrogen bonded to the free oxygen atoms of the bridging sulfate ions. The Cu atom and the 4,4'-bipyridyl are at general positions; the apparent local 2-fold through the Cu atom and the apparent inversion center in the 4,4'-bipyridine are not symmetry elements of the parent  $(2, c)$  structure. The S atoms of sulfates on 2-fold axes at  $0, 0, 1/4$  and its equivalents in the parent structure become three inequivalent sites. The inversion center of the terephthalic acids at  $1/2, 0, 0$  and its equivalents in the parent structure also become inequivalent. There are 32 symmetry elements ( $C2/c$  modulo  $2a_p, 2b_p, c_p$ ), thirty-two Cu atoms, thirty-two 4,4'-bipyridine ligands, sixteen sulfate ligands and sixteen terephthalic acid molecules in the expanded parent unit cell. The asymmetric unit thus contains four Cu atoms, four 4,4'-bipyridine ligands, two sulfate ligands and two terephthalic acid molecules.

A  $(3+1)$  dimensional approach, modulation vector  $(a_p^* - b_p^*)/2$ , suggests the possibility of a twinned triclinic crystal but observations of 37 weak reflections with  $h$  even,  $k$  even,  $h-k=4n-2$ , preclude this option. A  $(3+2)$  dimensional approach with modulation vector  $a_p^*/2, b_p^*/2$  allows for space group  $C2/c$  with four options for the selection of the quarter of the parent structure symmetry elements to be retained. Reverting to the standard setting four origin options for the asymmetric unit are allowed, but only two correspond to alternative origins for the asymmetric unit of the parent structure. In the correct model, the terephthalic acids no longer sit on inversion centers. Residual disorder about a 2-fold axis remains but an ordered structure in a lower symmetry space group was shown to be inappropriate.

The diffraction intensities show strong systematic dependence, dividing the data into three distinct groups: 2327 data with  $h=\text{even}, k=\text{even}, h-k=4n$  (78% observed), 37 data with  $h=\text{even}, k=\text{even}, h-k=4n+2$  (1% observed), and 2659  $h=\text{odd}, k=\text{odd}, h-k=2n$  (45% observed). The scattering density can be divided into four symmetrized components related to these intensity classes, such that  $\rho_{A1}(\mathbf{r})$  contributes only to the  $h=\text{even}, k=\text{even}, h-k=4n$ , contributes only to  $h=\text{even}, k=\text{even}, h-k=4n+2$ , and  $\rho_{A2}(\mathbf{r})$  and  $\rho_{B1}(\mathbf{r})$   $h=\text{odd}, k=\text{odd}, h-k=2n$  with the consequence that component  $\rho_{A2}(\mathbf{r})$  cannot be reliably determined from the data set.

**References:** (1). Rae, A. D. (2000) RAELS00, Australian National University, Canberra, Australia.

**Keywords:** crystallography, pseudo symmetry, commensurate modulation, modulated structure, group theory analysis