

PROVING COTTON'S CONJECTURE ON PENTACHROMIUM(II)
EXTENDED METAL ATOM CHAINS

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Extended Metal Atom Chains (EMACs) are a wide family of complexes consisting of ≥ 3 metal ions arranged in a central column and helically wrapped by organic ligands. This structure often leads to short metal-metal distances and promotes the formation of metal-metal bonds.^[1] Cr²⁺-based EMACs are of special interest, since they can exhibit intriguing physical properties such as single-molecule magnetic behaviour as well as strong electronic communication between the metal centers.^[2] However, their geometrical and electronic features (including the extent of bond delocalization) have long been contested. In particular, the arrangement of Cr²⁺ ions in [Cr₅(tpda)₄X₂] has been a core topic in this debate [X = SCN⁻ (**1**) or Cl⁻ (**2**); H₂tpda = N²,N⁶-di(pyridin-2-yl)pyridine-2,6-diamine].^[2] In 1999, Peng's group claimed a nearly uniform spacing of Cr²⁺ ions (2.24–2.28 Å) in **1** and 2·2Et₂O·4CHCl₃.^[3] However, the distinctly prolate shape of displacement ellipsoids for the 2nd and 4th metal in 2·CH₂Cl₂ led Cotton *et al.* to conjecture an unresolved disorder of unsymmetric chains, with alternating short (*d*_<) and long (*d*_>) Cr–Cr separations.^[4] Recent DFT calculations have lent support to this hypothesis, indicating that the unsymmetric forms of **1** and **2** are more stable than the symmetric ones by 1.7 and 2.9 kcal mol⁻¹, respectively.^[2] Here, we provide definitive proof of Cotton's conjecture by presenting single crystal X-ray data collected on **1** down to 3 K, where the thermal vibrations almost vanish (Fig. 1). According to our new data, the crystals are not tetragonal (*I4/m*), as originally reported by Peng *et al.*,^[3] but monoclinic (*C2/c*) with *a* ≈ *c* and β ≈ 90°. Refinement with two twin domains (≈1:1) linked by a 90° rotation along *y* reveals an ordered, clearly unsymmetric structure, with *d*_< and *d*_> differing by up to ~0.5 Å.

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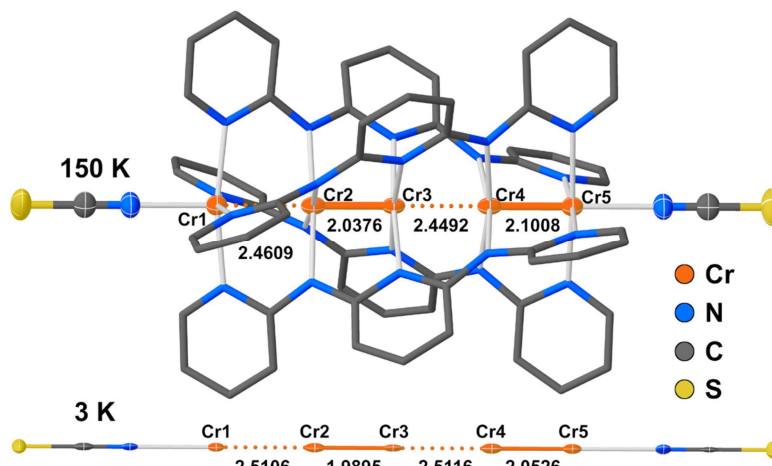


Figure 1. Structure of **1** at 150 and 3 K (thermal ellipsoids are set at 50% probability level). H atoms and (in the 3 K structure) tpda²⁻ ligands are omitted.

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