

Crystal engineering or crystal mysticism? A case study

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The de novo design and synthesis of a crystalline motif of a substance is a holy grail for a growing number of organic and inorganic synthetic chemists. Achievement of targeted architectural arrangements is less reliable as the complexity increases. Simple substitution of, for example, alkyl pendant groups with homologues¹ are most prone to success. Enthusiasts in this area have dubbed this evolving realm of research as 'crystal engineering,'² and 'reticular chemistry,' as "...the practice of logical synthesis must begin with knowledge of the target network 'blueprint' and identification of the required building blocks for its assembly. The process is central to our ability to achieve true design of solid state materials: we refer to its implementation as reticular chemistry."³ The flurry of activity has led to a plethora of fascinating new structures and materials, many conferences, symposia, monographs, and scientific papers in all of the leading journals, not to mention a glut of new jargon.

While I have been proclaimed to be, but do not consider myself, a 'crystal engineer,' we design, synthesize, and characterize new families of molecule-based magnets. Magnetic ordering is the clear and singular objective, but a specific 3-D structural motif of the targeted material has to be designed and synthesized - or 'crystal engineered.'

Paddle wheel-structured (D_{4h}) ruthenium acetate, $\text{Ru}_2(\text{O}_2\text{CMe})_4$, **1**, was identified as a key component to establish a new family of molecule-based magnets due to: (a) its cation, $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$, 1^+ , having three unpaired electron spins that are essential, but not sufficient, for achieving magnet ordering, and (b) 1^+ possessing one vacant coordination site per Ru to build an extended structure, **2**.⁴ To balance the charge, anionic $[\text{Cr}(\text{CN})_6]^{3-}$ was selected as it can bond to six $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^{+}$'s *via* the cyanide nitrogens to form a charge

compensated network structure. Thus, the structure of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ was 'crystal engineered' to be cubic ($a \sim 13.3 \text{ \AA}$), as well as magnetically ordered.



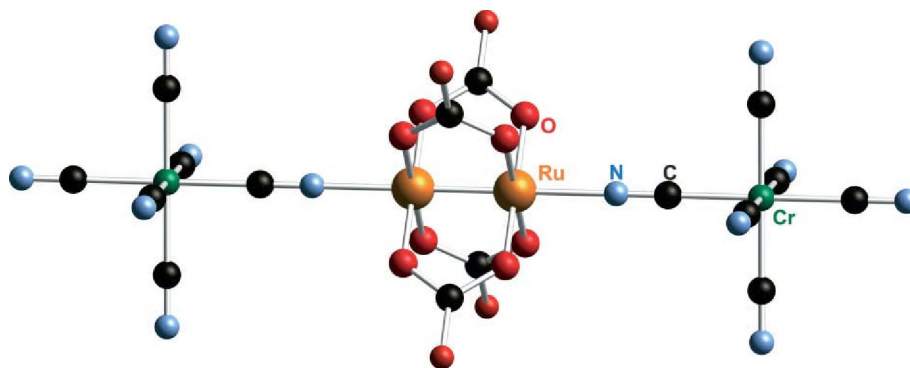
1, Paddle wheel-structured ruthenium acetate, $\text{Ru}_2(\text{O}_2\text{CMe})_4$ (Hs not depicted)

$[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ prepared *via* an aqueous reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]\text{Cl}$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$ successfully led to the formation of the sought cubic, 3-D extended structure (Fig. 1a).⁴ It must be noted that at our level of crystal engineering (or reticular chemistry) we failed to anticipate the presence of a second interpenetrating lattice (Fig. 1b), as confirmed from the Reitveld analysis of the synchrotron powder X-ray diffraction data and density measurements.⁴ Unintended consequences can fill clairvoyant voids.

In addition to a successful example of structure design and synthesis, *i.e.* 'crystal engineering,' not only was the predicted extended network structure obtained, but the material magnetically ordered at 33 K as a ferrimagnet,⁴ as desired.

Fueled⁵ by this crystal engineering success, we targeted making the pivalate analog, as replacement of the methyl group by the *tert*-butyl group should block formation of the second interpenetrating network, while maintaining the cubic motif. Modeling of the void volume and shape by the

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2, $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$ bridging two $[\text{Cr}(\text{CN})_6]^{3-}$ anions along one axis of a cube (Hs not depicted)

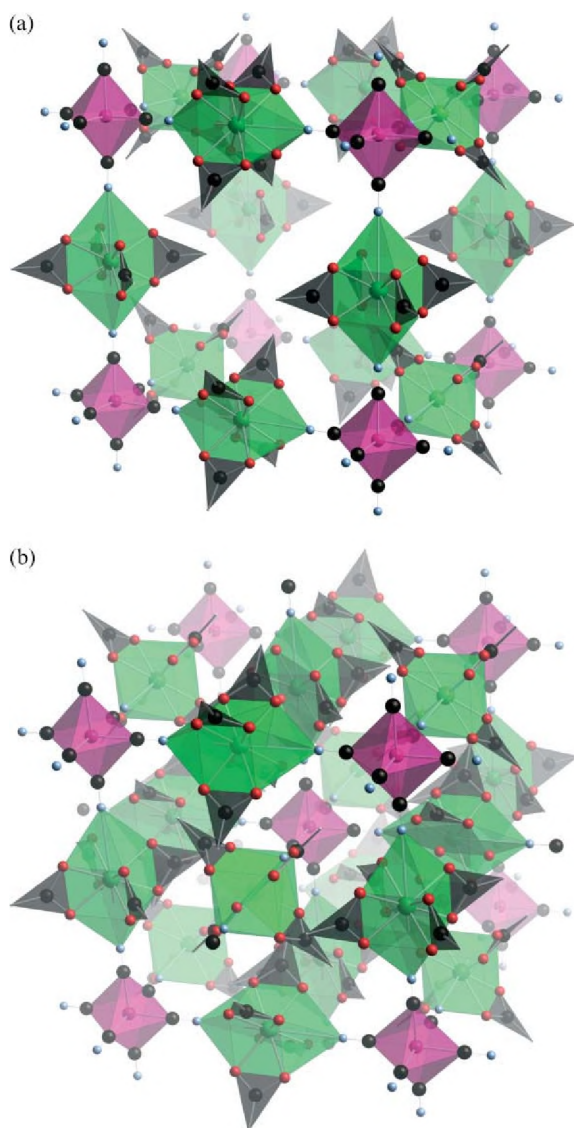


Fig. 1 Single, noninterpenetrating $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ cubic lattice (a), and the observed interpenetrating $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}(\text{CN})_6]$ cubic lattices (b).

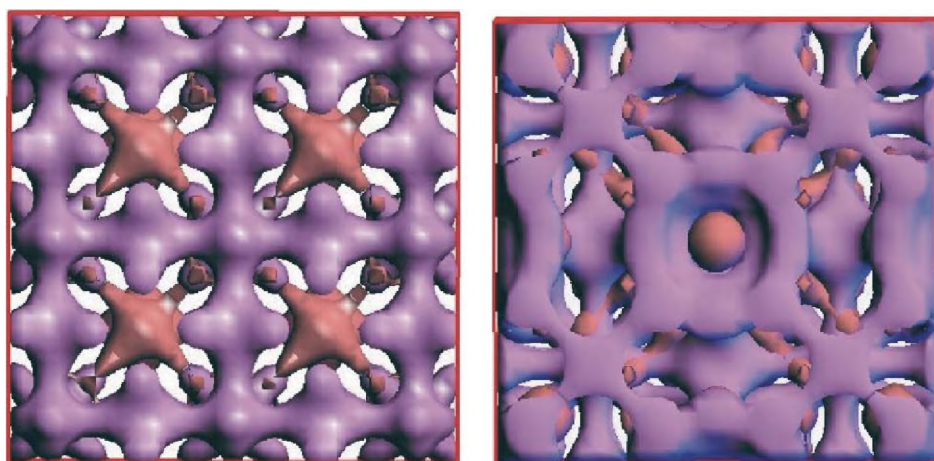


Fig. 2 Calculated void space (pink) for noninterpenetrating $[\text{Ru}_2(\text{O}_2\text{CR})_4]_3[\text{Cr}(\text{CN})_6]$ (purple) [R = Me (left); *tert*-Bu (right)].

isosurface method⁶ indicated that both cubic lattices were stable, Fig. 2.

Hence, $[\text{Ru}_2(\text{O}_2\text{C}^i\text{Bu})_4]_3[\text{Cr}(\text{CN})_6]$ was anticipated to form a cubic, noninterpenetrating lattice. Nonetheless, Yoshioka *et al.* reported that $[\text{Ru}_2(\text{O}_2\text{C}^i\text{Bu})_4]_3[\text{M}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ [M = Co, Fe] formed a layered (2-D) (Fig. 3),⁷ not cubic (3-D) network structure.

$[\text{Ru}_2(\text{O}_2\text{C}^i\text{Bu})_4]_3[\text{Cr}(\text{CN})_6]$ was prepared and its layered structure was verified to be isomorphous to the layered, 2-D motifs observed by Yoshioka *et al.*⁷ (as well as magnetically ordered).⁸ Thus, the relatively minor structural modification of replacement of an alkyl group with another alkyl group has a profound effect on the resultant structural architecture that eluded even the simplest of crystal engineering predictions.⁹ Alternatively, it is a failed example of ‘reticular chemistry,’ as while cubic $[\text{Ru}_2(\text{O}_2\text{C}^i\text{Bu})_4]_3[\text{Cr}(\text{CN})_6]$ is targeted *via* a logical synthesis based upon well-established precedent using the required building blocks, it is not achieved. Hence, ancillary pendant groups are an important consideration in designing extended structures.

Hence, as substantial progress is being made worldwide in the prognostication of crystal structures, the underlying scientific principles governing crystal structure, polymorph, and pseudo polymorph prediction and synthesis need to be reliably established to a greater extent than they have evolved so far. Thus, while we move along the learning curve toward the reliable design and synthesis of targeted chemical architectures with specific chemical and/or physical properties, we must benefit and learn as well as expect setbacks with crystal mysticism to hone our ability to design and prepare lattices with specific structures and properties. The ability to form or avoid and thus control interpenetrating structures is a goal that needs to be mastered. Fabricating materials with different and multiple interpenetrating lattices would enable the design of substances with combinations of properties leading to important new classes of hybrid multifunctional materials. Also, the controlled filling of void spaces with specific guests, solvent, and/or counterions is undeniably another area where synthetic proficiency is essential. In this vein, development of user-friendly software enabling the

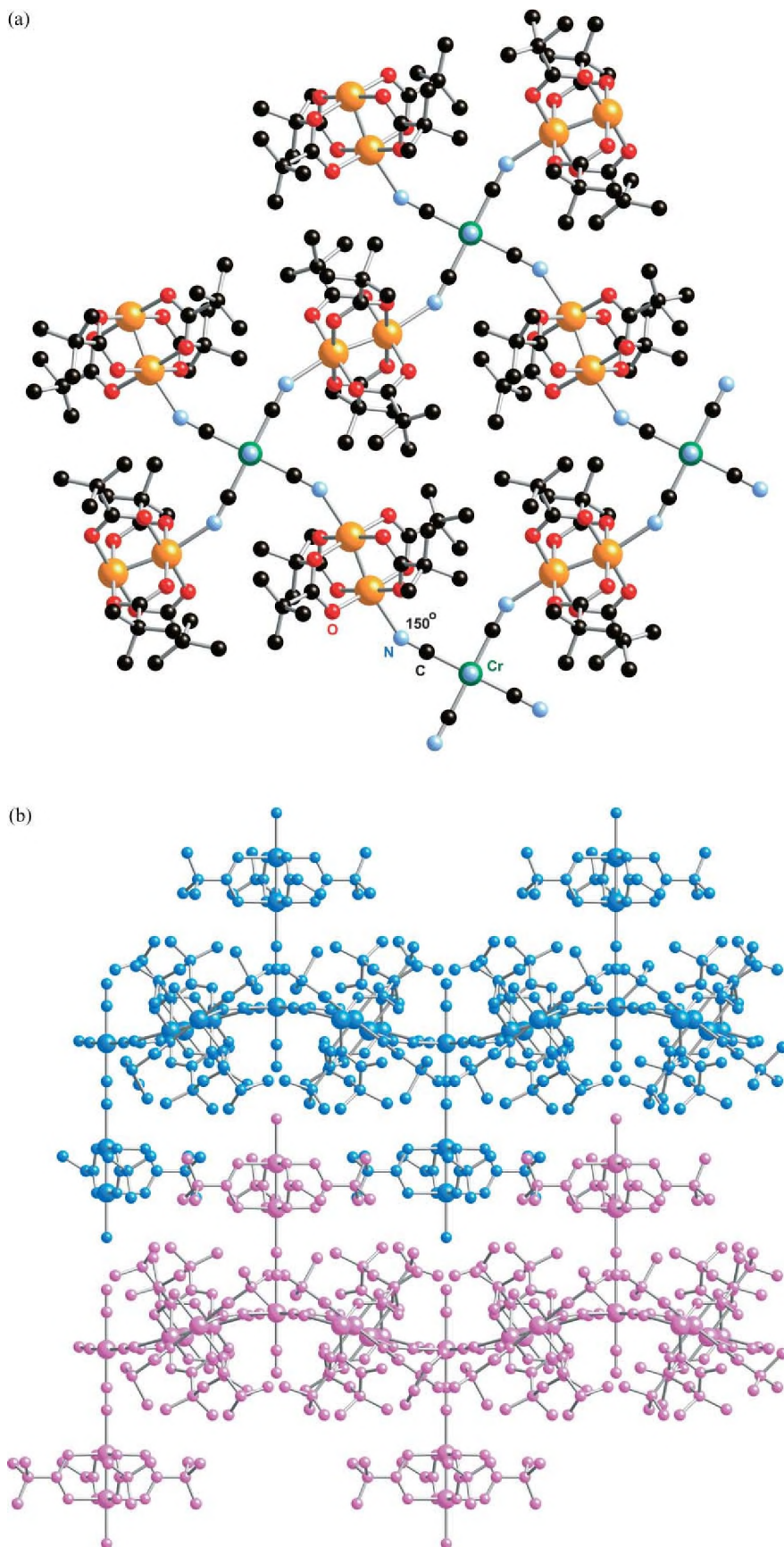


Fig. 3 Top view of layered (2-D) $[\text{Ru}_2(\text{O}_2\text{CBu}')_4]_3[\text{Cr}(\text{CN})_6]$ (top), and side view of layered (2-D) $[\text{Ru}_2(\text{O}_2\text{CBu}')_4]_3[\text{Cr}(\text{CN})_6]$ showing adjacent (pink and blue) layers (bottom). Reprinted with permission from Wiley-VCH *Angew. Chem. Int. Ed.* **44**, 2416–2419 (2005) [ref. 8].

identification of viable options for filling unit cell void space with guests, solvent, and/or counterions would be immensely valuable to synthetic chemists.

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