

tartrate, was carried out in 1951 by Bijvoet, Peerdeman and van Bommel using a Weissenberg camera and a specially constructed zirconium X-ray tube ($\lambda = 0.786 \text{ \AA}$, i.e. close to the Rb K-absorption edge at 0.865 \AA to enhance the anomalous scattering) [4]. This type of direct comparison of Bijvoet pairs or the application of the Hamilton R-factor ratio test [5], were the principal crystallographic techniques used to assign absolute structures until Rogers' introduction of the eta parameter into the least-squares refinement [6]. The Rogers eta parameter was quickly superseded by the Flack "x" parameter [7], a least-squares parameter which treated the crystal as a mixture of the original enantiomer and its twin by inversion. Flack pointed out that where as the Rogers parameter (which varied between +1 and -1) had no physical meaning as it approached the mid-point, zero, the Flack parameter x had a physical meaning over its entire range (from 0 to 1). A Flack parameter somewhere near the middle of the range, and with a suitable small e.s.d., indicated that the sample was twinned by inversion.

The incorporation of this parameter into most refinement programs, its ease of use, and its apparent robustness to less-than-ideal data collection strategies contributed to its rapid acceptance, and to misunderstandings about its interpretation. In 2000, almost 20 years after the Flack parameter was first described, Flack and Bernardinelli described the statistical interpretation of the parameter [8]. In spite of this, there continued to be a hunch amongst practical crystallographers that Flack's own interpretation of his parameter was unduly pessimistic. The publication of the derivation of the Hooft, Straver and Spek parameter in 2008 encouraged us to carry out a critical analysis of 150 samples of known absolute configuration, only light atoms and measured with molybdenum radiation [9]. Inspired by these results and prevalent urban myths, we have further studied some practical aspects that influence determination of the absolute structure.

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Pairwise assembly of high-nuclearity arylpalladium(II) cages

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Developments in palladium chemistry have led to the discovery of the excellent catalytic properties of a range of palladium complexes. The renowned capability of palladium to form sigma Pd-C bonds, which is frequently succeeded by the formation of C=C bonds in industrial applications, has been investigated in this research, and novel palladium cages with cyanuric acid bridging ligands have been synthesised and characterised. Ortho-metallated 2-phenylpyridinate (ppy⁻) and dimethylbenzylamine (BDMA⁻) -derived cages have both been studied.

For the 2-phenylpyridine ligands, the reaction of the parent dimer [Pd(ppy)Cl]₂ with cyanuric acid, in the presence of triethylamine, yields a decanuclear palladacycle [Pd₁₀(ppy)₁₀(C₃N₃O₃)₂(C₃N₃O₃H)₂], and a dodecanuclear palladacycle [Pd₁₂(ppy)₁₂(C₃N₃O₃)₄]. Single crystal x-

ray diffraction patterns for both compounds highlight the impact of the reduction in symmetry by removal of a dimer, with monoclinic symmetry ($C 2/c$) for the decanuclear structure and hexagonal symmetry ($P 6_3$) for the dodecanuclear structure. The stability of the dodecanuclear palladacycle has resulted in its formation during the synthesis using the correct stoichiometry for the dodecanuclear species **as well as** formation as the majority product in the synthesis using the stoichiometry for the decanuclear species. In-situ NMR studies have demonstrated the thermodynamic stability of the dodecanuclear palladacycle with irreversible conversion of the minority product [Pd₁₀(ppy)₁₀(C₃N₃O₃)₂(C₃N₃O₃H)₂] to the dodecanuclear structure by heating to 85 °C for three hours. The influence of solvent systems in the crystal structure of [Pd₁₂(ppy)₁₂(C₃N₃O₃)₄] is also interesting to note, as the space group varies from hexagonal $P6_3$ in chloroform and methanol to monoclinic $P2_1/a$ in chloroform and 1-octanol.

The ortho-metallated dimethylbenzylamine analogue [Pd₁₂(BDMA⁻)₁₂(C₃N₃O₃)₄] (previously characterised) exhibits improved solubility in contrast with [Pd₁₂(ppy)₁₂(C₃N₃O₃)₄] and this is attributed to the packing of the planar units of the latter hindering the facile formation of the latter cage. The presence of both enantiomers of the former cage renders the overall crystal structure racemic, whereas the latter cage is chiral.

Keywords: chirality, organometallic, palladium

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Synthesis and characterization of honeycombed ruthenium-based coordination polymers

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High-dimensional metal-organic coordination polymers have drawn considerable attention owing to their intriguing molecular topologies and their potential applications in catalysis [1], non-linear optics [2], host-guest chemistry [3] and the molecule-based magnetic materials [4]. A common approach for the design of such materials is the closing of multi-dentate ligands containing N- or/and O-donor atoms. Oxalate (ox) is an important ligand due to its various bridging abilities and strong coordinating tendency with transition metals to form 2- and 3-D frameworks. Several works [5], [6], using [M^{III}(ox)₃]³⁻ as unit building block from the combination with other metallic species, such as alkali monocations (Li⁺, Na⁺) or dicationic transition metal ions (Mn²⁺, Ni²⁺, Fe²⁺), have obtained two- and three-dimensional networks. These bimetallic anionic networks have the general formula {A⁺, [M^IM^{III}(ox)₃]^{x-}}_n; they can be described as being composed of an anionic honeycomb sublattice [M^IM^{III}(ox)₃]^{x-} and a cationic counterpart (A⁺)_n. The charge of each repeating unit of the anionic sublattice is one or two depending on the oxidation states of the metal centers.

In the present work, we explore the synthesis of new family of three-dimensional oxalate-bridged networks using [Ru(ox)₃]³⁻ as anionic bricks and [Ni(bpy)₃]²⁺/[Fe(bpy)₃]²⁺ (bpy = 4,4-bipyridine) as template cations. Single crystal and powder X-ray diffraction studies were performed. These compounds crystallize in the chiral cubic space group $P2_13$. They show the 3D chiral structure formed by Li⁺/Na⁺ and Ru³⁺ ions connected through oxalate anions with [Ni(bpy)₃]²⁺/[Fe(bpy)₃]²⁺ cations in the holes of the honeycombed network. The isolated solids have been characterized by IR spectroscopy and thermogravimetric methods (TG, DSC, DTA). A decomposition of ruthenium oxalate-based polymers beginning at 400 °C.

The reported compounds show catalytic activity in the CO₂ photoreduction to CO and formic acid at room temperature.