

St-Petersbur, (Russia). ^b*Swiss-Norwegian Beamlines at the ESRF, 38000 Grenoble (France).* ^c*Technische Universitat Braunschweig, 38106 Braunschweig (Germany).* ^d*Helmholtz Zentrum Geesthacht, 21502 Geesthacht (Germany).* E-mail: grigor@pnpi.spb.ru.

The X-ray and polarized neutron diffraction are used to determine the crystal handedness and magnetic chirality of the series of high-purity MnSi single crystals and mixed compounds crystals of $Mn_{1-x}Fe_xSi$ and $Fe_{1-x}Co_xSi$ grown by Czochralski methods [1,2]. To test the possibility to control the crystal handedness of the single crystals we have performed the following experiments with the crystal growth using Czochralski technique. (i) Using as a seed the right-handed crystal $Fe_{1-x}Co_xSi$ with $x = 0.10$ we have grown one series of $Fe_{1-x}Co_xSi$ samples with $x = 0.10, 0.15, 0.20, 0.25, 0.30, 0.50$. (ii) Using as a seed the left-handed crystal with $x = 0.50$ we have grown another series of $Fe_{1-x}Co_xSi$ samples again of different concentrations. The result of these experiments aimed to demonstrate whether handedness of these crystals depends on the concentration of Co, or, it is solely determined by the seed used for this synthesis. The third option could be if the handedness would not depend on a seed and/or concentration x .

In 90% cases the grown sample has been found to be enantiopure and to inherit the crystallographic chirality of its seed crystal. In 10% cases undefined circumstances flip the chirality over for the next progeny or produce a racemic sample. We demonstrate that (i) left and right forms of all transition metal monosilicides can be grown by the Czochralski method, (ii) the magnetic chirality of all $Mn_{1-x}Fe_xSi$ crystals follows its crystallographic counterpart [1], (iii) the opposite coupling between the crystal handedness and the spin chirality has been found for $Fe_{1-x}Co_xSi$ compounds [2].

Knowing the rigid coupling between the structural handedness and magnetic chirality we used the polarised neutron diffraction to indirectly determine the average handedness of six different polycrystalline samples of MnSi with large number of crystallites (100 crystals per cm^3). The average chirality of these polycrystals deviates unexpectedly high from zero. This net chirality is maybe related to the yet poor statistics in the numbers of the left or right crystallites inside the polycrystals.

[1] S.V. Grigoriev, D. Chernyshov, V.A. Dyadkin, V. Dmitriev, S.V. Maleyev, E.V. Moskvina, D. Lamago, Th. Wolf, D. Menzel, J. Schoenes, H. Eckerlebe, *Phys. Rev. B*, **2010**, *81*, 012408. [2] S.V. Grigoriev, D. Chernyshov, V.A. Dyadkin, V. Dmitriev, S.V. Maleyev, E.V. Moskvina, D. Menzel, J. Schoenes, H. Eckerlebe, *Phys. Rev. Lett.* **2009**, *102*, 037204.

Keywords: chirality, silicide, magnetism

MS87.P05

Acta Cryst. (2011) **A67**, C749

Non-centrosymmetric molecules - centrosymmetric structure?

Christophe M.L. Vande Velde,^a Matthias Zeller,^b Frank Blockhuys,^c ^a*Karel de Grote University College, Dept. of Applied Sciences,* ^b*Youngstown State University, Dept. of Chemistry,* ^c*University of Antwerp, Dept. of Chemistry. (Belgium).* E-mail: christophe.vandavelde@kdg.be

It is recognized that macroscopically centrosymmetric crystal structures can still give rise to NLO phenomena, due to growth-induced polarization [1]. We can take this one step further, and look at molecules which conformationally, due to their synthesis, inherently are a mixture of centrosymmetric and non-centrosymmetric forms. If the conformational differences are very small, one would in such a case normally come to expect a completely disordered, centrosymmetric crystal structure.

The compound being discussed in this contribution, a double

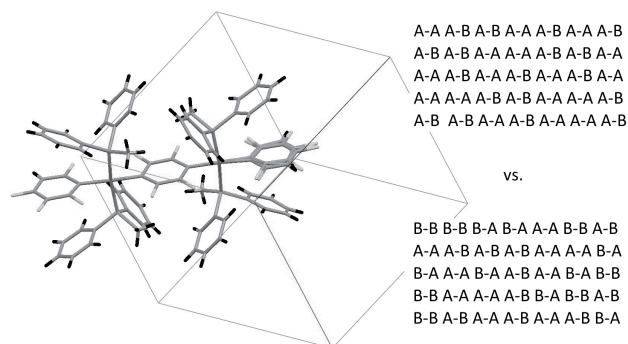
square planar Ni-phenylene complex [2] with 2,3,4,6-F-substituted phenyl rings that are unable to rotate once they bind to the complex, is ideally suited for this kind of study.

At first sight the compound indeed crystallizes in the space group P-1. We will explore the possibilities for experimentally exposing by x-ray crystallography the presence or absence of additional ordering within the crystal by way of growth-induced polarization, as well as the crystallization possibilities that such a substance really has.

These crystallization options for an A-A/A-B type compound consist of either a homogeneous, centrosymmetric, completely disordered structure (see figure, bottom); a racemic twin (i.e. polarization) with a (slight) preference for a particular orientation of one of the two rings; or else what is in fact a completely ordered structure on the molecular level, only allowing for disorder due to the statistical distribution of the second fluorinated ring. This would lead to the existence of large, completely ordered racemic twin domains within the crystal (see figure, top).

The presence or absence of this latter phenomenon would provide details on the process of crystal growth in this particular case.

We will here present the results, which indicate that centrosymmetry is not always what it appears to be at first sight. We have been able to deduce perfect ordering in the growth direction by re-examining different fragments of the same crystal, thus demonstrating that the resulting twin components are different in different regions of the same crystal, and that one ring is in fact completely ordered in domains that are macroscopic.



[1] J. Hulliger, H. Bebie, S. Kluge, A. Quintel, *Chem. Mater.* **2002**, *14*, 1523-1529. [2] K.C. Sturge, A.D. Hunter, R. McDonald, B.D. Santarsiero, *Organometallics* **1992**, *11*, 3056-3062.

Keywords: centrosymmetry, twinning, organometallics

MS87.P06

Acta Cryst. (2011) **A67**, C749-C750

Influencing absolute structure determination

Amber L. Thompson, *Chemical Crystallography, Chemistry Research Laboratory, Oxford (UK).* E-mail: amber.thompson@chem.ox.ac.uk

It is well established that the different enantiomers of a chiral material can have significantly different physiological properties. There are many well known, often quoted examples including the terpenes limonene & carvone [1], and the pharmaceuticals ibuprofen, naproxen and thalidomide [2]. As a consequence of this, drug manufacturers and drug authorisation authorities are increasingly concerned about the absolute configuration of active pharmaceutical ingredients. There are a number of "sporting" techniques, but one of the most relied upon is X-ray structure analysis [3], which in appropriate cases can give very reliable results.

The first absolute structure determination, of sodium rubidium

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.

[1] H.J. Bouwmeester, J. Gershenzon, M.C.J.M. Konings, R. Croteau, *Plant Physiol.* **1998**, *117*, 901-912. [2] G.L. Anderson, *J. Chem. Educ.* **2004**, *81*(7), 971-974. [3] A.L. Thompson, D.J. Watkin, *Tet. Asymm.* **2009**, *20*, 712-717. [4] J.M. Bijvoet, A.F. Peerdeman, A.J. van Bommel, *Nature (London)*, **1951**, *168*, 271-273. [5] W.C. Hamilton, *Acta Cryst.* **1965**, *18*, 502-510. [6] D. Rodgers, *Acta Cryst.*, **1981**, *A37*, 734-741. [7] H.D. Flack, *Acta Cryst.* **1983**, *A39*, 876-881. [8] H.D. Flack, G. Bernardinelli, *J. Appl. Cryst.* **2000**, *33*, 1143-1148. [9] A.L. Thompson, D.J. Watkin, *J. Appl. Cryst.* submitted.

Keywords: chirality, absolute structure, bijvoet

MS87.P07

Acta Cryst. (2011) **A67**, C750

Pairwise assembly of high-nuclearity arylpalladium(II) cages

C. Murray,^{a,b} A. Swift,^a H.M. Colquhoun,^a C.J. Cardin,^a D.Allan,^b
^a*Department of Chemistry, University of Reading, Reading, (UK).*
^b*Diamond Light Source Ltd, Didcot, Oxfordshire, (UK).* E-mail: c.a.murray@pgr.reading.ac.uk

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

MS87.P08

Acta Cryst. (2011) **A67**, C750-C751

Synthesis and characterization of honeycombed ruthenium-based coordination polymers

Alla Dikhtiarenko, Sergei A. Khainakov, José R. García, José Gimeno, *Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Oviedo (Spain).* E-mail: dikhtiarenkoalla@uniovi.es

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]³⁻}_n; they can be described as being composed of an anionic honeycomb sublattice [M^IM^{III}(ox)₃]³⁻_n 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.