

MS23-P10 Chiral aggregation hierarchy in high-pressure resolved 2-butanol and 2,3-butanediol Marcin Podsiadło, Ewa Patyk, Andrzej Katrusiak *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
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For decades separation of enantiomorphs has become increasingly important in pharmaceutical and fine-chemicals industries. However, no general rules allowing one to predict racemic or enantiomorphic crystallization are known. The rule formulated by Wallach in 1895,¹ that the density of enantiomorphs is lower than that of corresponding racemates, was based on eight enantiomorph-racemate pairs, of which one was an exception to the rule. It was concluded that the rule is fulfilled for most of compounds. Presently we investigate the effect of pressure on simple model compounds spontaneously forming enantiomorphic crystals at ambient pressure.

High-pressure isochoric freezing of (±)-2-butanol and (±)-2,3-butanediol yields enantiomorphic conglomerates, both of orthorhombic space-group $P2_12_12_1$ with isostructural OH...O bonding patterns. Despite the volume compressed two orders of magnitude more than expected from the Wallach's rule, the crystallization of racemates has not been enforced. Two stages of aggregation, the first through OH...O bonding of molecules into helical chains and sheets and the second through van der Waals and electrostatic interactions association of the chains and sheets into the 3-dimensional structures, have been distinguished. Each of these stages of aggregation favours the crystallization of enantiomers. The aggregation of enantiomorphic 2-butanol and 2,3-butanediol molecules into helices and chiral sheets is favoured sterically. The steric and electrostatic interactions explain the lack of pressure effect for enforcing the crystallization of 2-butanol and 2,3-butanediol, and invalidates the Wallach's rule for these compounds. Also sterical effects explain the aggregation of helices in enantiomorphic crystals.

[1] Wallach, O. (1895). *Liebigs Ann. Chem.* **286**, 90–143.

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MS23-P11 Challenges in small molecule XRD – Alkali Metal Organics from Ammonia. Reent Michel,^a Dietmar Stalke,^a *Institut für Anorganische Chemie der Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany*
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Ammonia as donating solvent is known for at least one century, but ammonia as donorbase in aggregates of organometallic compounds is a new and unknown class of compounds. Due to its volatility, the crystallographic investigation of these compounds faces problems with rapid decomposition of the material outside the mother liquor. Especially the application of thin plates and needle shaped crystals require special techniques in crystal mounting. Twinning, which stands outside the normal procedure, and disorder make organometallic ammoniacates to a challenging field in crystallography.

Lithium cyclopentadienyl derivatives are one of the most applied starting materials in metal organic synthesis. They are compounds *par excellence* to generate a huge variety of sandwich or half-sandwich d-block metal organics via transmetalation or salt elimination reactions. We have shown recently that addition of ammonia to THF generates lithocene or even naked Cp anions [1]. The strong donating and deaggregating properties of ammonia observed herein are the most likely reason for the high reaction rate of many organometallic species in liquid ammonia. The use of ammonia can be the key for reactions with a high potential barrier caused by steric repulsion. In contrast to reactivity enhancing additives like TMEDA or PMDETA the absence of a hydrocarbon skeleton can improve the performance of many reactions and generate H-bonded networks in the solid [2].

Usage of higher alkali metals and derivatives of Cp like CpMe, Cp*, indene and fluorene opens the door to a wide range of aggregates. In each case one particular aspect like the size of the cation, the donating properties of ammonia or the steric and electronic properties of the carbanion plays a key role within the structure.

[1] Michel, R., Herbst-Irmer, R., D. Stalke, D. (2010). *Organometallics* **29**, 6169-6171.

[2] Michel, R., Herbst-Irmer, R., D. Stalke, D. (2011). *Organometallics* **30**, 4379-4386.

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