



INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

# **Creating Optical Activity**

## **Total Spontaneous Resolution and Viedma Ripening**

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Akademisk avhandling för filosofie doktorsexamen i Naturvetenskap, inriktning kemi, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredag den 10 november 2017 kl. 10.00 i SB-H1, Sven Hultins Gata 6, Johanneberg campus, institutionen för kemi och molekylärbiologi, Göteborg.

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## Abstract

The creation of optical activity has been considered as something impossible even though reports of such creation via total spontaneous resolution since the 1940's have been published. More recently Viedma ripening have been developed that also produce enantiopure bulk product. Both methods are examples of absolute asymmetric synthesis i.e. the synthesis of optically active product from non-optically active starting materials, catalysts or auxiliaries.

In this work twenty-four new compounds have been synthesized, isolated and characterized with X-ray diffraction. Out of these have eleven been found to crystallize as conglomerates as chiral enantiopure crystals which are optically active. The discovered conglomerates have been analyzed with solid state techniques as circular dichroism (CD) and vibrational circular dichroism (VCD).

For the moderately labile  $[\text{Ru}(\text{PS})_2\text{Cl}_2]$ ,  $[\text{Ru}(\text{dmsO})_2(\text{NS})\text{Cl}_2]$  and  $[\text{Ru}(\text{dmsO})_2(\text{SS})\text{Cl}_2]$  have the chirality been fixated by oxidizing the ligand in solution to the corresponding sulfoxide. For the highly labile  $[\text{Co}(\text{bpy})_3](\text{PF}_6)_2$  the chirality has been fixated by oxidizing the metal from cobalt(II), solvent free in the solid state, to the inert cobalt (III) with bromine vapor or solid iodine. The optical activity of the inert complexes has been analyzed with solution techniques such as CD, HPLC and ORD.

The optical activity of the complexes  $[\text{Mo}(\text{CO})_4\text{PS}]$  and  $[\text{W}(\text{CO})_4\text{PS}]$  have been analyzed with solid state VCD with less than tenth of a milligram sample and high-quality spectra have been obtained in 20 minutes.

Total spontaneous resolution has been achieved with the compounds  $[\text{Ru}(\text{PS})_2\text{Cl}_2]$ ,  $[\text{Ru}(\text{dmsO})_2(\text{NS})\text{Cl}_2]$ ,  $[\text{Ru}(\text{dmsO})_2(\text{SS})\text{Cl}_2]$  and  $[\text{Ag}(\text{PS})_2](\text{BF}_4)$  in good yield and high *ee*.

Viedma ripening has been demonstrated for the complexes  $[\text{Ag}(\text{PS})_2](\text{BF}_4)$ ,  $[\text{Mo}(\text{CO})_4\text{PS}]$ ,  $[\text{W}(\text{CO})_4\text{PS}]$  and  $[\text{Cu}(\text{mtp})_2(\text{NO}_3)_2]$ . Viedma ripening has been found to be viable for the production of large quantities of optically pure metal complex.

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**Keywords:** Optical activity, absolute asymmetric synthesis, total spontaneous resolution, Viedma ripening, grinding, chirality, conglomerate, coordination compound, coordination polymer, single crystal X-ray diffraction, solvent free oxidation, enantioselective sulfide oxidation, solid state VCD.