Synthesis of a Werner-type Tetrahedral Chiral-at-Cobalt(II) Complex with an Achiral Unsymmetric Tridentate Ligand

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Chiral metal complexes show promises for asymmetric catalysis, chiroptical devices and so on. Most of them are synthesized by combining carefully tuned chiral ligands with metal salts or organometallic reagents. On the other hand, since Werner studied the chiral cobalt complexes, it is well known that overall chirality can also be generated from the stereogenic metal center. The synthesis of such chiral-at-metal complexes is a useful method for constructing a new chiral metal complex structure without the need for any chiral ligands in the coordination sphere of the metal center. There are many examples of octahedral and half-sandwich shaped chiral complexes, but due to the rapid racemization, few tetrahedral chiral-at-metal complexes have been reported.

Recently, our group reported a tetrahedral chiral-at-zinc complex with high enantiopurity and its catalytic application.¹ Herein we report the synthesis of a redox-active, tetrahedral chiral-at-cobalt(II) complex with an achiral unsymmetric tridentate ligand.

First, $Co(N(SiMe_3)_2)_2$ was prepared by mixing anhydrous $CoCl_2$ and $LiN(SiMe_3)_2$ in Et₂O. The mixture was then mixed with H₂L and subsequently precipitated to afford a dinuclear cobalt-lithium complex 1 in 90% yield. X-ray diffraction analysis revealed that the relative configurations of the two metal centers are fixed in the crystal state. Next, by adding 'BuCN and crystallizing, *racemic* [CoL('BuCN)] was obtained in 56% yield. A slightly distorted tetrahedral structure was confirmed by X-ray diffraction. We are currently in the process of optical resolution with a chiral auxiliary. In this presentation, the synthesis, structural details, and electrochemical properties of this cobalt complex will be discussed.



¹ K. Endo, et al. Nat. Commun. 2020, 11, 6263.