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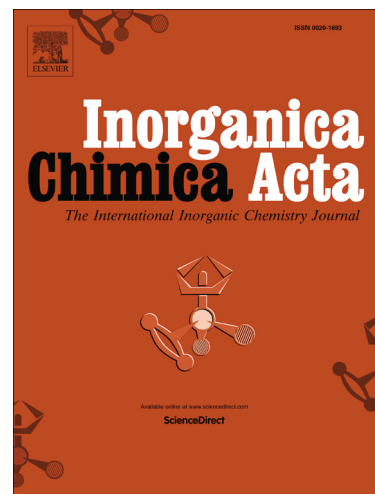
PII: S0020-1693(18)30726-6  
DOI: <https://doi.org/10.1016/j.ica.2018.06.044>  
Reference: ICA 18336

To appear in: *Inorganica Chimica Acta*

Received Date: 10 May 2018  
Revised Date: 24 June 2018  
Accepted Date: 26 June 2018

Please cite this article as: X-D. Zheng, Y-L. Huang, Y-P. Tong, A pair of homochiral complexes generated via spontaneous resolution: synthesis, structures and dielectric properties, *Inorganica Chimica Acta* (2018), doi: <https://doi.org/10.1016/j.ica.2018.06.044>

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# A pair of homochiral complexes generated via spontaneous resolution: synthesis, structures and dielectric properties

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## ARTICLE INFO

### Article history:

Received

Received in revised form

Accepted

Available online

### Keywords:

Homochiral Complexes

Spontaneous Resolution

Dielectric Property

## ABSTRACT

Spontaneous resolution occurred during the reactions of racemic macrocyclic compound  $[\text{Ni}(\text{rac-L})](\text{ClO}_4)_2$  with  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  in DMF (acetone diffusion), and a pair of novel homochiral coordination complexes  $\{\text{Ni}(\text{SS-L})[\text{Fe}(\text{CN})_5\text{NO}]\text{DMF}\}$  (**SS-1**) and  $\{\text{Ni}(\text{RR-L})[\text{Fe}(\text{CN})_5\text{NO}]\text{DMF}\}$  (**RR-1**, L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane, DMF = N,N-Dimethylformamide) as racemic conglomerate were immediately obtained. While the same reaction solution ( $[\text{Ni}(\text{rac-L})](\text{ClO}_4)_2$  with  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  in DMF) produced the racemic compound of  $\{[\text{Ni}(\text{rac-L})][\text{cis-Fe}(\text{CN})_5\text{NO}]\}_2$  (**meso-1**) [41] when volatilized naturally in the air for about 4 days. The phase purity of the compounds has been confirmed by X-ray powder diffraction patterns. Meanwhile, the solvent effect of the reactions, as well as the thermal stability, CD spectra, and dielectric property of the compounds were investigated.

## 1. Introduction

Chirality is an essential feature in nature process and life system and is also of great significance in advanced materials [1-7]. Recently, increasing importance has been attached to the research of producing chiral metal-organic materials, because this class of chiral hybrid inorganic/organic compounds usually possess of special properties such as photoluminescent, magnetic, ferroelectric and dielectric properties, and even show their possible applications in nonlinear optics, asymmetric catalysis, enantioselective separation, etc [8-16]. Though a good deal of chiral metal-organic materials have been reported until now, the exploration for how to control the absolute conformation of chirality in a molecular structure to acquire enantiopure chiral compounds is still an appealing challenge [11, 17-20].

There are three general approaches for constructing homochiral metal-organic materials. The most effective and most popular approach is using an enantiopure ligand, which by chiral conservation will give the same handedness to the final framework [21-24]. The second approach uses achiral precursors, which can be induced by the chiral agent during the generation process to form a homochiral structure. This approach also needs an enantiopure chiral agent, which can be a chiral catalyst, a chiral solvent, or an enantiopure chiral auxiliary ligand that does not directly participate in the formation of the framework [25-31]. However, because of the limitation of the chiral pool and very often the high cost of chiral ligands, as well as the possibility of in situ ligand racemization during the framework formation, it is highly desirable to create chiral compounds from achiral or racemic precursors without any chiral condition. Thus, the third approach, which constructing a homochiral compound from totally achiral starting precursors without any chiral source via spontaneous resolution arises and be highly regarded [32-40].

Although it is well known that supramolecular interactions, such as metal ligand coordination interactions, hydrogen bonding, and  $\pi$ - $\pi$  interactions, play a very important role in the assembly process, spontaneous resolution of metal coordination compounds is still rather rare in chiral synthesis. As spontaneous resolution is unpredictable, and the process is hard to control. Among the spontaneous

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