

Mononuclear Valence Tautomeric Cobalt Complexes Bearing Enantiopure Ligands for Polar Space Groups and Helical Morphology

程, 豊

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氏 名 : 程 豊

論 文 名 : Mononuclear Valence Tautomeric Cobalt Complexes Bearing
Enantiopure Ligands for Polar Space Groups and Helical Morphology
(エナンチオピュア配位子を有するコバルト原子価異性錯体の極性構
造とヘリカル形態)

区 分 : 甲

論 文 内 容 の 要 旨

If materials with spontaneous polarization are capable of polarization changes in response to external stimuli, such changes are often accompanied by pyroelectric currents or voltages and can be used in sensors, capacitors, and storage devices. Dynamic molecular crystals are a class of crystals that can switch between two or more physical properties, such as magnetic, conductive, ferroelectric, optical, mechanical, and polarization capabilities, in response to external stimuli such as light, magnetic fields, pressure, temperature, and X-rays. For each structural unit in a crystal, changes in molecular structure or charge distribution, etc. will inevitably lead to changes in molecular dipole moments, and if such molecules can be arranged in a polar space group, the dipole moments between molecules will not be able to cancel each other out, thus allowing the crystal to possess spontaneous polarization in a specific direction. As a special class of dynamic molecular crystals, valence tautomeric (VT) compounds are a class of complexes that undergo electron transfer in response to external stimuli, such as heat, light, pressure, magnetic fields, etc. By crystallizing the VT complexes in the polar space group, the accompanying VT transition will lead to a change in the polarization of the crystals. Therefore, to obtain VT complexes that can achieve polarization conversion in response to external stimuli, it is most important to obtain VT compounds that can crystallize in polar space groups. Based on this, a new strategy to enable VT compounds to crystallize in the polar space group was devised in this thesis, i.e., by introducing enantiopure ligand into the complex, thus making the probability of the complex crystallizing in the polar space group much higher.

On the other hand, the introduction of chiral ligands has been surprisingly found to influence the morphology of certain VT compounds, forming helices with specific chirality. The transfer of such chirality from the molecular level to the macroscopic morphology is reminiscent of DNA and proteins. At the same time, VT compounds are able to switch between two states, similar to 0 and 1 in binary, and each VT molecule can be considered as a storage unit. Based on this, VT complexes self-assemble to form helices with storage potential, which is somehow similar to the formation process and function of DNA. Therefore, the exploration of related systems will lead to a better understanding of certain biological processes, as well as bionanotechnology.

In **chapter 2**, two different crystals of racemic VT compounds $[\text{Co}(\text{3,5-dbdiox})_2\text{Rac-L}]$

•dioxane (*Rac-1*) and $[\text{Co}(\text{3,6-dbdiox})_2\text{Rac-L}] \cdot \text{dioxane}$ (*Rac-2*) (3,5-dbdiox = 3,5-di-*tert*-butylcatecholate (3,5-dbcate) or 3,5-di-*tert*-butylsemiquinonate (3,5-dbsq); 3,6-dbdiox = 3,6-di-*tert*-butylcatecholate (3,6-dbcate) or 3,6-di-*tert*-butylsemiquinonate (3,6-dbsq); *Rac-L* = racemic *N, N, N, N*-tetramethyl-1,2-diphenylethylenediamine) were synthesized, and both of them show VT transitions. The bond length variations of *Rac-1*/*Rac-2* at high and low temperatures was studied by crystal structures, which suggest a typical temperature-dependent VT transition. Meanwhile, *Rac-1* and *Rac-2* crystallizes in the centrosymmetric space groups $P2_1/c$ and $C2/c$, resulting in the crystal with a macroscopic polarization of 0. The VT transition of *Rac-1*/*Rac-2* was further confirmed by IR absorption spectra and magnetic susceptibility.

For the **chapter 3**, a series of mononuclear Co complexes bearing enantiopure ligands were synthesized, namely, $[\text{Co}(\text{3,5-dbdiox})_2\text{RR-L}] \cdot \text{dioxane}$ (*RR-1*) and $[\text{Co}(\text{3,5-dbdiox})_2\text{SS-L}] \cdot \text{dioxane}$ (*SS-1*), $[\text{Co}(\text{3,6-dbdiox})_2\text{RR-L}] \cdot \text{dioxane}$ (*RR-2*) and $[\text{Co}(\text{3,6-dbdiox})_2\text{SS-L}] \cdot \text{dioxane}$ (*SS-2*), $\text{Co}(\text{3,6-dbdiox})_2\text{RR-L} \cdot \text{MeCN}$ (*RR-3*) and $[\text{Co}(\text{3,6-dbdiox})_2\text{SS-L}] \cdot \text{MeCN}$ (*SS-3*), $[\text{Co}(\text{3,5-dbdiox})_2\text{RR-L}_1] \cdot \text{dioxane}$ (*RR-4*), $[\text{Co}(\text{3,5-dbdiox})_2\text{RR-L}_1]$ (*RR-5*). All the crystal structures were determined at low temperature and high temperature to examine bond length variations, which suggest all of them possesses typical temperature-dependent VT transition. They possess different VT transition temperatures and crystallize in different space groups, where *SS-1/RR-1*, *RR-4*, *RR-5* crystallize in the polar space groups $P2_1$, $P2_1$, $C2$, respectively, while *SS-2/RR-2*, *SS-3/RR-3* crystallize in the piezoelectric space groups $C222_1$ and $P2_12_12_1$, respectively. The VT transition features of *SS-1/RR-1*, *SS-2/RR-2*, *SS-3/RR-3*, *RR-4* and *RR-5* were further validated by IR absorption spectra and magnetic susceptibility. *SS-1/RR-1* was used as a representative to introduce in detail the macroscopic polarization changes of the complex crystals by the introduction of enantiopure ligands.

For the **chapter 4**, two mononuclear complexes $[\text{Co}(\text{3,6-dbdiox})_2\text{SS-L}] \cdot \text{dioxane}$ and $[\text{Co}(\text{3,6-dbdiox})_2\text{RR-L}] \cdot \text{dioxane}$ in the presence of *SS-1/RR-1/Rac-1*, can develop into helices (*SS-6/RR-6*) with specified chirality. According to IR spectra and PXRD analysis, *SS-6/RR-6* has the same chemical formula and crystal structure as *SS-2/RR-2*. To investigate the conditions for the formation of helical crystals, mixtures of *SS-1/RR-1/Rac-1* and *SS-2/RR-2* in different ratios and concentrations were used to obtain crystals by solution diffusion, all of which formed helices of different sizes. Simultaneously, the solution mixing of *SS-1/RR-1* and *Rac-2* can gently twist the crystal to produce a particular chiral helix. The special chemical, physical, and mechanical properties originated from the functional groups' transition from random distribution to exact arrangement around an axis which can be used in nature to create structural and functional materials, such as chemical energy storage, transmembrane proteins, connective tissue, and genetic information storage. This discovery will assist in the understanding of various biological processes in nature as well as the creation of bionic devices.

This thesis focuses on exploring two special properties possessed by VT compounds bearing enantiopure chiral ligands, i.e., higher probability of crystallization in the polar space group compared to normal VT compounds and expression of chirality in macroscopic morphology. Both of these topics are related to the expression of chiral small molecules to macroscopic processes, and at the same time, they belong to different research systems.