

Helical, Nonracemic Inorganic–Organic Hybrid Polymers of Cadmium Halides with Pentadentate Bis(oxazoline) Ligands

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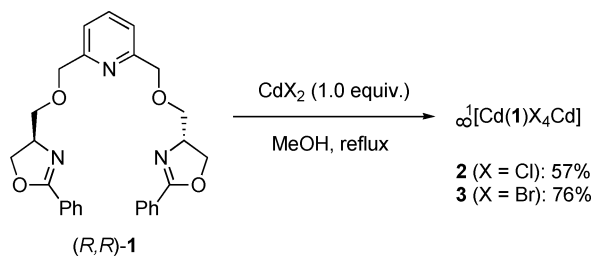
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Helical, nonracemic structures play a fundamental role in many natural systems, perhaps most prominently represented by α -helical polypeptides or double-stranded helices of nucleic acids. In recent years, much effort has been devoted to the controlled construction of inorganic coordination compounds with enantiopure topology, stimulated by their potential impact on important areas of research like enantioselective catalysis, molecular recognition, etc. Although predetermination of chirality in mononuclear metal complexes is quite common today,¹ the extension to polymeric metal–organic coordination compounds remains challenging. In the field of coordination polymers² (infinitely extending metal–ligand assemblies with bridging organic ligands), induction of nonracemic helicity is known in only a few cases. In contrast, the domain of inorganic–organic hybrid polymers³ (metal centers, modified by organic ligands and connected by inorganic bridges) has seen only very recently a first example of the generation of an enantiopure, one-dimensional helical chain with a chiral M–O–M subnetwork.⁴

We recently reported chiral, C_2 -symmetric pentadentate bis(oxazoline) ligands for the stereoselective transfer of carbon-centered, tetrahedral chirality to metal centers with various coordination geometries, thereby creating metal complexes with predetermined helicity.⁵ Extending this concept from the creation of mononuclear species to the construction of polymeric structures led us to investigate the corresponding cadmium halide species, known for their tendency to form halogen bridged one- and two-dimensional assemblies.⁶

The synthesis of the complexes proved to be straightforward (Scheme 1). Refluxing equimolar amounts of CdX_2 and the novel ligand **1** in methanol resulted in colorless precipitates, isolated in analytically pure form by a simple filtration and drying in vacuo.

Scheme 1



The two compounds were only poorly (**2**) or slightly soluble (**3**) in CH_3CN . The species in solution are most probably mononuclear, such as $[Cd(1)X]^+$ and $[CdX_3]^-$, also supported by mass spectrometry (ESI-MS). Despite the low solubility, it was possible to obtain 1H NMR and ^{13}C NMR spectra in CD_3CN , clearly showing only one species and a downfield shift of most of the well-resolved signals, indicative of strong complexation. In addition, the C_2 -symmetry of the free ligand is preserved in the complexes, as could be deduced from the number of signals in the NMR spectra.⁷ The

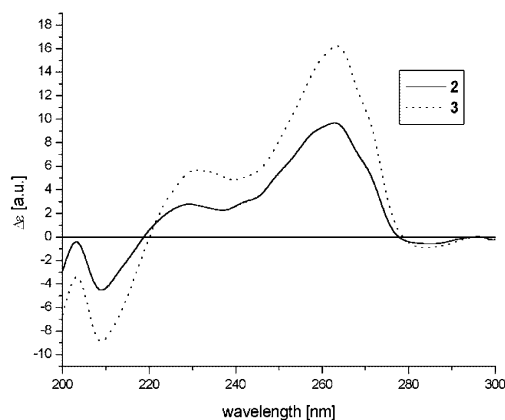


Figure 1. CD spectra for **2** and **3** in CH_3CN .

complexes are not stable in DMF or DMSO, yielding NMR spectra identical to the spectrum of the free ligand.

To investigate the structure of the species in solution further, especially the stereoselectivity of the complexation, CD spectra were recorded in CH_3CN (Figure 1). **2** and **3** show essentially the same spectra, exhibiting positive peaks for the $n-\pi^*$ transitions of the pyridine chromophore around 263 nm and a negative minimum at 209 nm. The shape is very characteristic for a pentagonal Λ_2 coordination geometry, as seen in a number of analogous mononuclear complexes of ligand **1**.⁸

Last but not least, it was possible to obtain crystals suitable for X-ray analysis by slow vapor diffusion of diethyl ether into a solution of the complexes in acetonitrile (Figures 2 and 3).⁹

The solid-state structures reflected all the results obtained in solution. In **2**, two unique formula units were found in the asymmetric unit, which differ, however, only slightly from each other. The structures of **2** and **3** are very similar and follow the same design principles.⁷ They consist of unprecedented one-dimensional chains of pentagonal-bipyramidal coordinated Cd centers, connected by only slightly distorted tetrahedral CdX_4 units

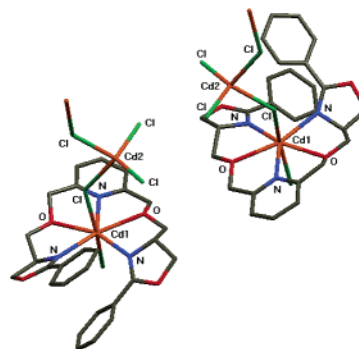


Figure 2. Asymmetric unit of **2** (two independent formula units present). Hydrogen atoms omitted for clarity.

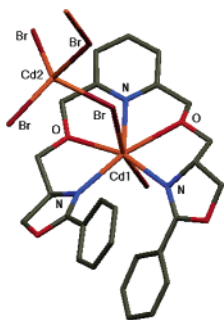


Figure 3. Asymmetric unit of **3**. Hydrogen atoms omitted for clarity.

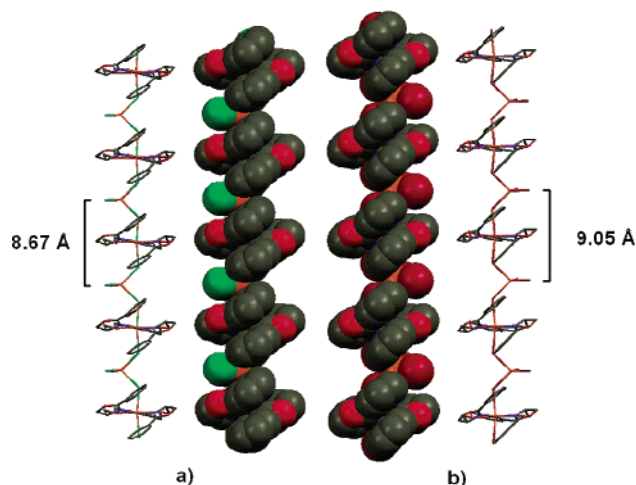


Figure 4. Part of the 1D chain subunits of (a) **2** and (b) **3**.

via bridging halogens (Figure 4). The inorganic Cd–(μ -X) backbone itself is achiral but accounts for the infinite polymeric character, while the helical structure is exclusively made up by the twist of the organic ligand. This is different from the previously known related examples for one-dimensional homochiral polymeric helices with an extended *chiral inorganic* subnetwork⁴ or *discrete* (μ -X)-bridged Cd centers infinitely connected by *organic* ligands²ⁱ and constitutes the novel aspect of the present compounds.

All bond lengths and angles are in the normal range. An obvious difference between the two structures is the increase in the helical pitch (8.67 Å for **2** vs 9.05 Å for **3**), resulting from the different bridging X–Cd bond length (Cd–Cl, 2.503–2.601 Å vs Cd–Br, 2.636–2.729 Å). Regarding stereochemistry, only Λ_2 -configured metal centers are present, yielding exclusively right-handed helical chains. The stacking of the individual chains is parallel to each other and to the crystallographic axis *a*, thereby creating a highly directed, helically ordered assembly. In both compounds, every other chain is stacked upside-down, resulting in a deviation of the connecting Cd tetrahedra alternately to the right and to the left with respect to the plane bisecting the pyridine ring. Obviously, this does not change the overall helicity of the assembly. In both cases, the columns are ordered in a zigzag fashion (in the plane normal to the axis *a*), and each neighboring chain is shifted by half of the helix pitch (normal to axis *b*) (Figure 5).

In conclusion, we have shown that the new multidentate ligand **1** is capable of inducing helical topology in inorganic–organic

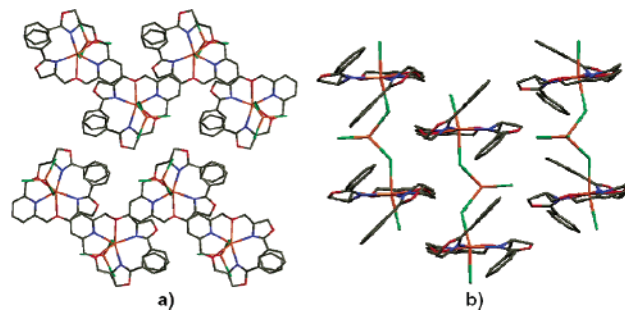


Figure 5. View normal to (a) the crystallographic axis *a* (along the chain axis) and (b) the axis *b* for **2** (in analogy for **3**).

hybrid polymers with unprecedented design and complete stereoselectivity. This constitutes, to the best of our knowledge, the first example of homochiral, nonracemic, one-dimensional helices with an infinite backbone exclusively made up by bridging halogens.

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Supporting Information Available: Experimental details for the preparation of **2** and **3**, as well as ¹H and ¹³C NMR spectra, CD spectra, and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- For more details, see the Supporting Information.
- For example, we have synthesized Λ_2 -[Fe^{II}(1)(H₂O)₂](ClO₄)₂, having pentagonal-bipyramidal geometry (X-ray) and exhibiting CD signals very similar to those of **2** and **3**.
- X-ray single-crystal diffraction data for **2** and **3** were collected on a STOE-IPDS diffractometer. Crystal data for **2**: C₂₇H₂₇Cd₂Cl₄N₃O₄ (824.24), colorless rod, monoclinic, space group *P2*₁, *a* = 8.6650(9) Å, *b* = 12.2190(8) Å, *c* = 29.130(3) Å, β = 95.297(12)°, *V* = 3071.0(5) Å³, *Z* = 4, ρ = 1.783 g·cm⁻³, μ (Mo K α) = 1.770 mm⁻¹, *T* = 173(1) K, *R*₁ = 0.0313, *wR*₂ = 0.0575, GOF = 0.826, abs. structure param. = 0.00(3). Crystal data for **3**: C₂₇H₂₇Br₄Cd₂N₃O₄ (1001.94), colorless prism, orthorhombic, space group *P2*₁2₁2₁, *a* = 9.0518(7) Å, *b* = 12.5611(7) Å, *c* = 29.0084(15) Å, *V* = 3298.3(4) Å³, *Z* = 4, ρ = 2.018 g·cm⁻³, μ (Mo K α) = 6.170 mm⁻¹, *T* = 173(1) K, *R*₁ = 0.0344, *wR*₂ = 0.0634, GOF = 0.820, abs. structure param. = -0.011(14).

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