

H-bonded polymerisation of alternate Δ and Λ metallohelicates

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Abstract: The neutral Cd^{II} complex Cd(HL)₂ (H₂L = 2-[(1H-imidazol-2-yl)methyleneamino]phenol) is chiral and it can be considered as a simple metalhelicite, with its corresponding Δ and Λ enantiomers. In the solid state, its helices are hierarchically assembled as a linear polymer, via mutual N-H...O interactions between each two alternating enantiomers, and which also are π - π stacked, so this polymer is based on a by a dimeric repeat unit $\{\Delta, \Lambda$ -[Cd(HL)₂]₂}.
Keywords: Chirality / H-bond / polymer / metalhelicite / self-assembly

Introduction

In the course of our investigations to pursue different Cd^{II} systems involving coordination with the Schiff base (*E*)-2-[(1H-imidazol-2-yl)methyleneamino]phenol (H₂L, Fig. 1), we have used different reaction conditions to obtain varied complexes as [Cd(HL)₂] or [Cd₁₀(L)₄(HL)₆(ClO₄)₂(CO₃)](ClO₄)₂ (Fig. 1).^[1] Although the impressive crystal structure of the decanuclear complex, had centred our attention at a first moment, we would like to analyse here the interesting crystal structure of the apparently simple [Cd(HL)₂], as one our research interests is the design not only of discrete metallohelicates, but as the more challenging design of superstructures based on metallohelic units.^[2]

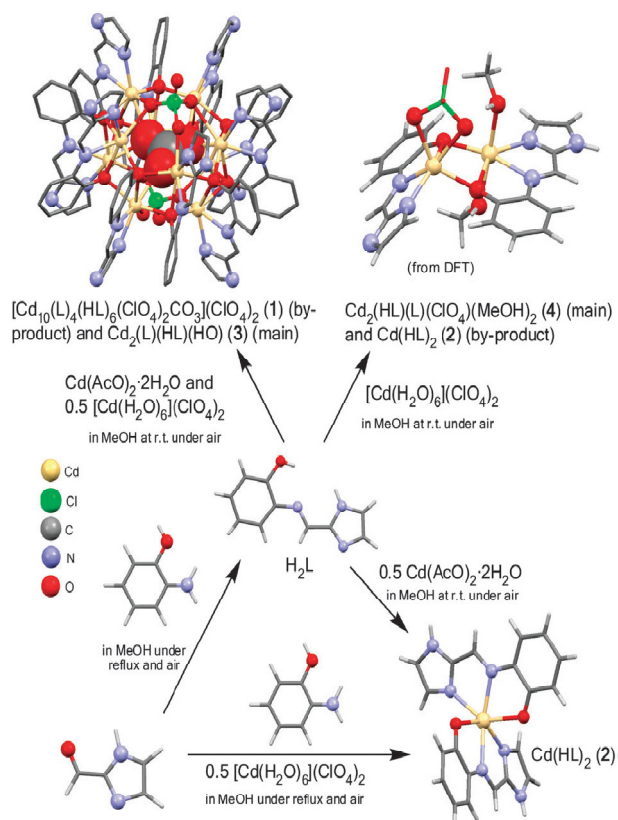


Fig. 1. Varied Cd^{II} complexes obtained from its interaction with H₂L using different reaction conditions. The crystal structure of [Cd(HL)₂] is shown right bottom, while the H₂L is in the centre of the figure.

Results and discussion

The asymmetry of the Schiff base H₂L, and the spatial arrangement adopted by the two ligands present in neutral Cd(HL)₂ units, where ligands are acting as monoanionic *O,N,N*-donors, leads to this complex to be helically chiral. Since the ligand is achiral, the complex is forming a typical Δ, Λ -racemate,^[3] which crystallises in the centrosymmetric *P*2₁/*n* group. The space-filling views showed in Fig. 2 allow

appreciating that Δ -Cd(HL)₂ strongly reminds to a simple two-blade propeller. To distinguish between both enantiomers, we have chosen as “head” the phenol residue, while the imidazole ring has been considered as the “tail” of the ligand.

Regarding to the geometric parameters, bond distances do not merit further comment, but angles around the cadmium(II) ion demonstrate a significant distortion of the pseudo- octahedral chromophore, being the O-Cd-O and N-Cd-N angles of *ca.* 98.9 and 110.9°, respectively.^[1]

An actually interesting feature of this complex in the solid state is the uncommon supramolecular arrangement of these cadmium helices, which are forming a singular 1D polymer (Fig. 3). Its infinite chains are formed by alternate Δ and Λ enantiomers coupled by means of mutual H bonds, and where the repeat unit of the polymer is a mesohelical Δ,Λ dimer. In addition, the double interaction between neighbor helices lead to ligands of contiguous complex units to be π - π stacked with a head-to-tail disposition .

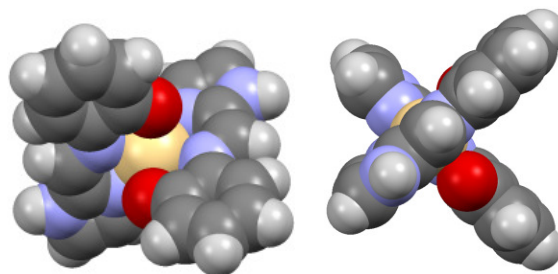


Fig. 2. Spacefilling views of the complex, with the two-blade propeller shown along its C_2 axis is shown at left.

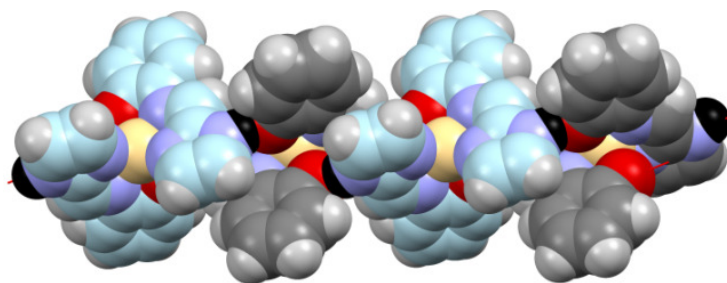


Fig. 3. Spacefilling (80%) representations of the linear polymer formed by both helical enantiomers of Cd(HL)₂. For a better understanding, the C atoms of the Λ enantiomer are blue coloured, while those of the Δ enantiomer are grey. The H atoms of the imidazol ring that mutually connect the molecules are black, while Cd atoms are pale yellow.

Thus, for each complex unit, both imidazole NH groups are acting as donors to two phenolate atoms of two contiguous complex units, and which are mirror images of the central one, while its two phenolate O atoms are reciprocally acting as acceptors for two imidazol N-H bonds of the two

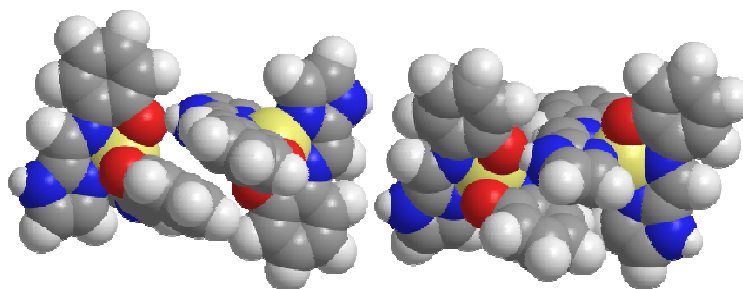
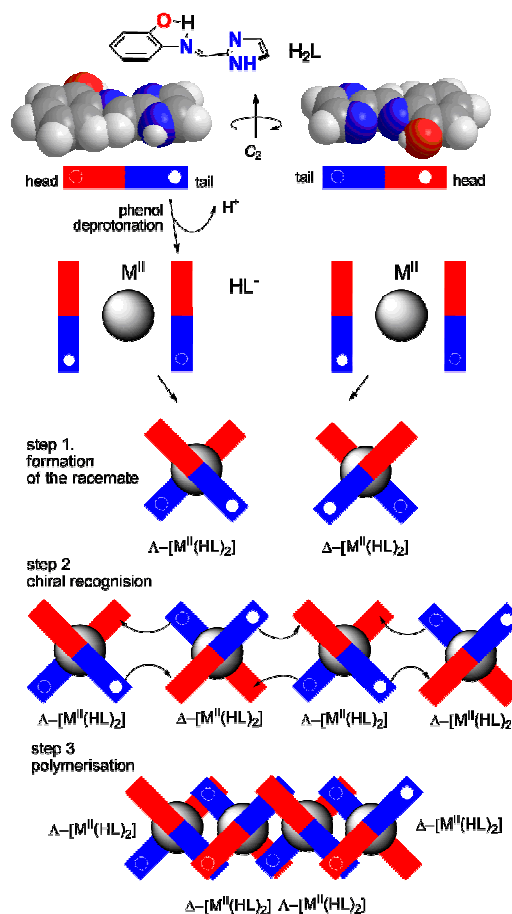


Fig. 4. The two possible dispositions for mutual NH-O interactions between two Λ enantiomers of Cd(HL)₂, since the ligands not involved in the H bonding scheme are differently orientated (head-to-head at right, head to tail at left). Both possibilities would display π,π - stacking, but the orientation of their respective N and O atoms is not adequate to form so many H bonds, as occurring when Δ and Λ enantiomers interact. These models are proposed on the basis of the same ligand arrangement found in the mesohelical polymer, so some hindrance could be avoided after a small rearrangement

neighbouring mirror $\text{Cd}(\text{HL})_2$ molecules. Therefore, each complex unit participates in four H bonds. Probably, the aperture of the ligands previously mentioned allows an easier access to the internal acceptor phenolate O atoms for the external N-H donor bonds.

Only head-to-tail interactions appear possible for $\text{Cd}(\text{HL})_2$, since only O phenol atoms can act as acceptors, and N-H bonds as donors. But, with the intention of understanding the mesohelical arrangement, we have simulated the rapprochement between homochiral helicates (Fig. 4). As a result, it appears that only one $\text{NH}\cdots\text{O}$ bond seems to be reasonable between two homochiral units, instead of the two occurring between each two contiguous heterochiral complexes of the mesohelical polymer. Therefore, this possibility appears less favourable than the mesohelical combination experimentally observed for $\text{Cd}(\text{HL})_2$. Consequently, this process requires a heterochiral but enantioselective recognition, as to join the next unit of the polymer is always preferred a mirror image of the last unit assembled.

This lineal assembly is hierarchical, and it is represented in Scheme 1. The first step is the formation of the Λ, Δ -racemate of mononuclear complexes. Then, the interaction between mirror enantiomers via mutual $\text{N-H}\cdots\text{O}$ bonds is enforced by the stacking of their ligand π systems, after heterochiral recognition.



Scheme 2. Hierarchical assembly of the neutral $\text{Cd}(\text{HL})_2$ helices to form the linear mesohelical polymer formed by alternate Δ and Λ isomers

Conclusion

We report here the spontaneous assembly of a novel polymer formed by pairs of alternate enantiomers via H-bonds and π - π stacking. The polymerisation process appears to be favoured between mirror isomers more than between equal enantiomers.

Experimental procedure

$\text{Cd}(\text{HL})_2 \cdot \text{H}_2\text{O}$ was obtained by stirring overnight a methanol solution (60 mL) containing H_2L (134 mg, 0.7 mmol) and $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (94 mg, 0.35 mmol), at room temperature. This gave a yellow powder, which was filtered off and dried in vacuum. Alternatively, this reaction could be performed under reflux for 5 h when imidazole-2-carboxaldehyde (80 mg, 0.8 mmol) and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (168 mg, 0.4 mmol) were

firstly mixed in methanol (50 mL) and then 2-aminophenol (87 mg, 0.8 mmol) was added to the resulting solution. Single crystals of Cd(HL)₂ were obtained from the mother liquor solution (methanol).

Yield: 66%; Elemental analysis calcd (%) for C₂₀H₁₈CdN₆O₃: C 47.8, H 3.6, N 16.7; found: C 47.5, H 3.4; N 16.8. MS (FAB⁺, MNBA): *m/z* (%): 485.1 (4) [Cd(HL)₂+H]⁺, 298.0 (4) [CdL+H]⁺; ¹H NMR (250 MHz, dms-*d*₆): δ 13.14 (br, 2H; NH), 8.62 (s, 2H; H-7), 7.43 (d, 2H, *J* = 7.6 Hz; H-5), 7.43 (br, 2H; H-9), 7.19 (br, 2H; H-10), 7.09 (t, 2H, *J* = 7.6 Hz; H-3), 6.82 (d, 2H, *J* = 7.6 Hz; H-2), 6.70 (t, 2H, *J* = 7.6 Hz; H-4); FTIR (KBr, cm⁻¹): ν(O-H_w) 3438 (m), ν(N-H) 3061(w), ν(C=N_{imine}) 1588(m).

Crystal data for Cd(HL)₂: (at 100(2) K): triclinic, *P* 2₁/*n* (No. 14), C₂₀H₁₆CdN₆O₂, *M*_w = 484.79, *a* = 9.0408(5) Å, *b* = 17.4676(9) Å, *c* = 11.6328(5) Å, β = 90.467(2); *V* = 1837.00(16) Å³, *Z* = 4; ρ_{calc} = 1.753 g·cm⁻³; *R*₁ = 0.0429 and *wR*₂ = 0.1095 (*I* > 2σ*I*), *R*₁ = 0.0646 and *wR*₂ = 0.1233 (all data), residual electron density 1.583 and -0.861 e- Å³ and.

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