A double-stranded dinuclear cadmium(II) helicate that assembles into chains in the solid state

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A [4+4] double-stranded cadmium dihelicate was afforded from an easily accessible thiosemicarbazone ligand; its crystal structure reveals the assembly of two enantiomers into dihelicate pairs, these pairs being further connected into infinite linear chains.

The assembly of metallo-supramolecular architectures from reactions of relatively simple ligands with suitable metal ions has attracted much interest over the last two decades[1]. Despite the intense investigation in this field, predicting the result products of a self-assembly process is still not trouble-free as it depends on numerous factors, such as the coordination, geometric preferences and size of the metal centres, the structure of the ligand strands or the existence of weak intra- or intermolecular non-covalent connections (e.g. hydrogen bonds or interactions between aromatic groups).[2]

Scheme 1 Pentadentate (left) and tetradentate (right) *bis*thiosemicarbazone ligands H_2L^X.

We have investigated the factors involved in the self-assembly of diverse supramolecular species by using tetra- and pentadentate *bis*thiosemicarbazone ligands as building blocks (Scheme 1). We probed that these ligands generate a novel fashionable structural motif, the cluster helicates, with silver(I) and copper(I) ions, while dihelicates or mesocates can be obtained from metal(II) ions, like Zn(II).[3]

Having these results in mind, we decided to test the interaction of the new tetradentate *bis*thiosemicarbazone ligand H_2L^{Ph} (Scheme 2) with the cadmium (II) ion. We have introduced a bencyl ring as spacer and as terminal group on the thiosemicarbazone threads of this ligand, with the aim to check whether the absence of donor groups in the spacer and the presence of bulky aromatic substituents in the binding domains affect the architecture of the complex formed.

Scheme 2 Ligand H_2L^{Ph}.

H_2L^{Ph} was easily prepared by condensation of 4-*N*-phenylthiosemicarbazide and 1,3-diacetylbenzene.‡ Electrochemical oxidation of a cadmium plate in a conducting suspension of H_2L^{Ph} produces a yellow solid, which was analytically and spectroscopically identified as $[Cd_2L^{Ph}{}_2]\cdot 2H_2O$ **1**.§ Recrystallization of this compound from acetonitrile by slow evaporation afforded yellow crystals of $[Cd_2L^{Ph}{}_2]\cdot 0.5CH_3CN$ **2**.γ

Fig. 1 Crystal structure of $[Cd_2L^{Ph}{}_2]\cdot 0.5CH_3CN$ **2**. Thermal ellipsoids at 50% probability. Solvent molecules and H atoms have been omitted for clarity.

The single-crystal diffraction analysis of **2** revealed that the asymmetric unit contains an unexpected cadmium (II) double-stranded dihelicate (Fig. 1). This neutral compound is constructed by two bideprotonated ligand units $(L^{Ph})^{2-}$ arranged around two cadmium atoms. Both enantiomers (P and M) are present in the crystal cell. The dihelicate is additionally solvated by half acetonitrile molecule.

The cadmium atoms adopt a distorted tetrahedral kernel by coordination with the imine nitrogen and the thioamide sulfur atoms belonging to two intertwined dianionic ligand threads. The existence of a distorted tetrahedral environment is indicated by the value of the metal-donor bond angles: S4-Cd1-S1 (146.70 (9)º), N3-Cd1-N10 (133.82(7)º), S2-Cd2-S3 (157.38(2)º) and N9-Cd2-N4 (124.43(7)º) are higher than the theorical value of 109.5º for an ideal tetrahedral geometry, whereas N10-Cd1-S4 (82.35(10)º), N3-Cd1-S1 (78.98(5)º), N4-Cd2-S2 (78.65(5)º) and N9-Cd2-S3 (78.08(5)º) are smaller.

The formation of a four-coordinated kernel is not common for Cd(II) complexes. This metal ion uses to adopt higher coordination numbers, six being the more frequent,[4-9] but five,[8,10] seven[6,11] and eight[11,12] are also possible. We have found in the literature only two examples with coordination index of four, which show square planar geometries around the metal centres.[13] To the best of our knowledge, a tetrahedral environment in Cd(II) helicates has not been found previously, therefore we can state that **2** is the first Cd(II) dihelicate with the metal ions tetrahedrally coordinated. It must be also noted that this complex is the first cadmium dihelicate derived from a thiosemicarbazone ligand. Previously, dinuclear dimers[3d,10] or mononuclear cadmium compounds[11] were obtained with this kind of ligands. The scarce examples of cadmium dihelicates found so far were mainly achieved with nitrogen donor systems.[4-6,12,14]

Our previous findings demonstrated that the absence of a donor atom in the spacer of the thiosemicarbazone ligands determined the assembly of the building blocks into a mesohelical architecture for metal(II) ions like Zn(II)[3c] and Co(II).[15] However, in the present study a double-stranded dihelicate was obtained instead. It seems that the size of the metal centre plays an important role in the arrangement of the ligands around the metal ions.

Fig. 2 Ball and stick representation of the enantiomers assembly into pairs through weak interactions.

Another additional interest of the **2** structure lies in its crystal packing. Thus, two dihelicate enantiomers are connected by Cd-S secondary bond interactions [Cd2···S3^i 3.1484(6) Å; -x, 2-y, 1-z], by intermolecular hydrogen bonds established between one of the thioamide nitrogen atoms as donor and one of the thioamide sulfur atoms as acceptor [N7-H7N···S2 3.586(2) Å; -x, 2-y, 1-z], as well as by edge-to-face CH···π interactions involving the terminal phenyl groups of the thiosemicarbazone threads [(C19-C24)$_{centroid}$···H29 3.890 Å]. As a result of these multiple contacts two enantiomers are assembled into dihelicate pairs (Fig. 2).

Every pair of enantiomers is further connected with a close pair, by the establishment of intermolecular hydrogen bonds engaging the remaining nitrogen and sulfur thioamide atoms [N1-H1N···S1 3.412(2) Å; 1-x, 2-y, -z], and an edge-to face CH···π contact involving the aromatic spacer from one tetranuclear unit and the terminal phenyl ring from a close enantiomer couple, the distance H37···centroid (C10-C15) being 3.278 Å. These interactions permit the assembly of the dihelical enantiomer pairs into infinite linear chains, with the individual enantiomers P and M occupying alternate positions along the packing (Fig. 3).[16]

Fig. 3 Self-assembly of the dihelical enantiomer pairs into an infinite linear chain.

This Cd(II) complex has been completely characterized[§], including ^{113}Cd NMR and luminescence studies. The ^{113}Cd NMR spectrum exhibits a signal at 529 ppm (Fig. S1[†]), value close to those found for Cd(II) complexes with [N_2S_2] coordination environments in DMSO solutions.[17] It has been established that an increase in the coordination number due to DMSO or water oxygen atoms would cause an important upfield of the signal (δ ^{113}Cd ~ 280 ppm).[17b] Therefore, the displacement observed in this spectrum points to the maintenance of the tetracoordinated kernel showed in the solid state.

The optical properties of the cadmium dihelicate were studied in acetonitrile solutions by UV-Vis and fluorescence spectroscopies. The UV-Vis spectrum (Fig. S2[†]) shows bands within the range 226-292 nm and at 330 nm, which can be ascribed to π-π* intraligand and LMCT transitions, respectively. The emission spectrum shows a broad weak emission band at 490 nm, when excited at 350 nm, which could be tentatively assigned to ligand-to-metal charge transfer transitions.

In summary, the complex herein reported constitutes a case of hierarchical assembly of helicates. Thus, an appropriate design of the ligand together wit a suitable choice of the metal centre permits the formation of a unique [4+4] double-stranded cadmium dihelicate, which at the same time assembles chains of enantiomers through the crystal lattices.

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[†] *Electronic Supplementary Information (ESI) available: [Fig. S1 ^{113}Cd NMR spectrum for **1** and Fig. S2 Fluorescence emission spectrum for **1**]. See DOI: 10.1039/b000000x/*

[‡] Experimental data for H_2L^{Ph}: The ligand bis(4-*N*-phenylthiosemicarbazone)-1,3-diacetylbenzene (H_2L^{Ph}) was prepared by condensation of 1,3-diacetylbenzene (0.73 g, 4.5 mmol) with 4-*N*-phenylthiosemicarbazide (1.11 g, 9 mmol) in absolute ethanol (200 mL) using acid catalysis. The solution was heated under reflux for 10 h and concentrated with a Dean Stark trap to *ca*. 40 mL. The white precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL) and dried *in vacuo*. Yield 1.23 g, 83%. MS (ESI-): m/z 459.0 for $\{HL^{Ph}\}^-$. Elemental analysis found: C, 62.6; H, 5.2; N, 18.6; S, 13.9; $C_{24}H_{24}N_6S_2$ requires: C, 62.6; H, 5.3; N, 18.3; S, 13.9 %. IR (KBr, cm^{-1}): ν(NH) 3379 m, 3342 w, 3263 w, ν(C=N) + ν(C−N) 1543 s, 1497 m, 1479 m, ν(C=S) 1113 m, 752 w, ν(N-N) 1028 w. ^{1}H NMR (dmso-d_6): δ 10.63 (s, 2H), 10.11 (s, 2H), 8.37 (s, 1H), 8.06 (d, 2H, 8.4 Hz), 7.52 (d, 4H, 7.7 Hz), 7.45 (t, 1H, 8.4), 7.34 (m, 4H, 7.7 and 6.6 Hz), 7.20 (t, 2H, 6.6 Hz), 2.43 (s, 6H). ^{13}C NMR (dmso-d_6): δ 177.04 (C=S), 149.04 (C=N), 139.12 (C_{ar}), 137.69 (C_{ar}), 128.30 (CH_{ar}), 128.07 (CH_{ar}), 127.92 (CH_{ar}), 125.78 (CH_{ar}), 125.34 (CH_{ar}), 125.03 (CH_{ar}), 14.79 (CH_3).

[§] Experimental data for **1**: The complex was obtained by means of an electrochemical method. The cell can be represented as Pt(–) | H_2L^{Ph} + MeCN | Cd(+). To a suspension of H_2L^{Ph} (0.1 g, 0.2 mmol) in acetonitrile (80 cm^3) was added a small amount of tetraethylammonium perchlorate as supporting electrolyte. The resulting mixture was electrolysed at 10 mA and 22 V for 1 h and 10 min. The obtained yellow powder was washed with diethyl ether and dried *in vacuo*. *Caution: Perchlorate salts are potentially explosive and should be handled with care. Yield 0.1 g (80%). MS (ESI+): m/z 573.1 $\{CdL^{Ph} + H\}^+$, 1141.8 $\{Cd_2L^{Ph}{}_2 + H\}^+$. Elemental analysis found: C, 48.3; H, 3.9; N, 14.1; S, 11.2. $C_{48}Cd_2H_{48}N_{12}S_4O_2$ requires C, 48.9; H, 4.1; N, 14.3; S, 10.9 %. IR (KBr, cm^{-1}): ν(OH) 3426 w, ν(NH) 3305w, ν(C=N) + ν(C−N) 1527 s, 1495 s, 1480 s, ν(C=S) 1117 w, 753 w, ν(N-N) 1032 w. ^{1}H NMR (dmso-d_6): 9.22 (s, 1H), 8.71 (s, 1H), 8.32 (s, 1H), 7.76 (d, 2H, 7.7 Hz), 7.60 (d, 2H, 7.7 Hz), 7.38 (d, 2H, 8.4 Hz), 7.27 (t, 1H, 8.4 Hz), 6.91 (m, 4H, 7.7 and 6.6 Hz), 6.76 (t, 2H, 6.6 Hz), 2.62 (s, 3H), 2.08 (s, 3H). ^{113}Cd NMR (dmso-d_6): δ 529 ppm. Uv-Vis [CH_3CN, λ_{max}] = 226, 234 (sh), 292, 330 nm.

[γ] Crystal structure analysis of **2**: X-ray diffraction data were collected from a yellow prismatic crystal (0.27 x 0.23 x 0.22 mm^3) by means of a BRUKER APPEX2 CCD diffractometer using graphite-monochromated

Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) from a fine-focus sealed-tube source. Crystal data for $C_{48}H_{44}Cd_2N_{12}S_4$, 0.5($C_2H_3N$): M_r=1162.58, T=100 (2) K, triclinic P-1, a=12.9413 (5), b=13.3757(4), c=14.5468(5) Å, α= 85.181(2), β=76.730(2), γ= 86.916(2)º, V=2440.59(15) Å^3, Z=2, ρ_{calcd}=1.582 g/cm^{-3}, μ=1.09 mm^{-1}, 60729 measured reflections, 11154 independent reflections (R_{int}=0.028), 9338 independent reflections with $I>2\sigma(I)$, 702 parameters refined, GOF=1.042, R_1=0.0287 ($I>2\sigma(I)$) and 0.0378 (for all data), R_{2w}=0.0648 ($I>2\sigma(I)$) and 0.0682 (for all data), max./min. residual electron density 0.937/-0.573 eÅ^{-3}; b) The crystal structure was solved by SIR-97[18] and refined by full-matrix least-squares procedures on F^2 using SHELX-97 software.[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms positions were included in the model by electronic density or were geometrically calculated and refined using a riding model; the structure presents a little disorder in a terminal fragment (S4-C42-N12-(C46-C48)) refined at 50% of probability and also in the MeCN solvent molecule; c) CCDC 742771 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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