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Metal self-recognition: a pathway to control the formation of dihelicates and mesocates[†]

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We have studied the factors that affect the formation of different metallosupramolecular architectures by metal direct self-assembly. A synthetic route has been developed to obtain mesocates or dihelicates selectively. For this purpose a series of five bisthiosemicarbazone ligands derived from 1,3-diacetylbenzene were designed and synthesised. Namely H_2L^{Me} , H_2L^{Et} , H_2L^{Ph} , H_2L^{PhN} and H_2L^{PhOMe} with different substituents on the 4-N terminal position of the thiosemicarbazone strands. The Co(II), Zn(II) and Cd(II) complexes of these ligands were prepared by an electrochemical procedure. Crystallographic studies revealed the formation of mesocates for Co(II) and Zn(II) metal ions whereas the Cd(II) complexes gave a bishelical supramolecular structure. Therefore these bisthiosemicarbazone ligands enable the selective isolation of mesocate or dihelicate complexes by using a specific metal ion.

Introduction

In the past two decades a great deal of attention has been paid to the self-assembly of metallosupramolecular architectures.^{1,2} Supramolecular aggregates of different shapes and functionalities have been obtained by using well-designed organic ligands in combination with appropriate metal ions or metal complex fragments.^{3–6} Among the wide set of multinuclear supramolecular systems, helicates are probably the most widely studied species^{1d,7} and are used as simple models to study the elemental principles that direct the self-assembly process. The study of helicates has shown that the specificity of the supramolecular self-assembly depends on the symmetry of the molecular components: *i.e.* the stereoelectronic preference of the metal ions and the arrangement of the binding sites in the precursor ligand.

A judicious choice of the bridging ligands and the metal ions is therefore crucial for the deliberate formation of helicates. With regard to the ligands, a minimum requirement seems to be that the binding sites must be disposed so that they could bridge two or more metal ions, otherwise simple mononuclear complexes may result.^{8,9} If this requirement is fulfilled, homochiral (Δ and Λ) helicates are formed as a racemic mixture if the achiral ligands are twisted around the metal ions.¹⁰ The side-by-side coordination of the ligands, however, results in achiral mesohelicates or mesocates, in which metal centres exhibit opposite chirality (Δ and Λ).

Helicates are being intensively studied because of their involvement in new areas of research such as anion sensors,¹¹ luminescence, magnetism, chirality, molecular machines,^{12,13} guest recognition and DNA binding.¹⁴ In contrast, mesocates have received significantly less attention, despite the great potential applications of these achiral structures, which include molecular wires and molecular switches to name but two examples in information storage and processing nanotechnology.¹⁵

The selective formation of either the helical or meso form has been a topic of debate since the first mesocate was reported by Albrecht in 1995.¹⁶ The formation of mesocates instead of helicates appears to be controlled by a variety of factors, including the particular ligand architecture, the variation of the metal and the incorporation of a guest molecule.

In a first approach, Albrecht *et al.* proposed the well-known *odd–even rule*, which states that the length of the alkyl spacer between two bidentate chelating units of the bridging ligand can determine whether the resulting complex will have a helical *(even)* or a meso-helical *(odd)* structure.^{17–20} However, Dolphin and co-workers demonstrated that this rule is not universal, because ligands with a single methylene spacer can form both diastereoisomeric species from the same reaction.²¹ The same group also investigated the interconversion between helicates and mesocates by changing reaction conditions such as solvent

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and temperature.²² It was found that bond rotation in the ligand allows the transition between the two conformers under the reaction conditions and this results in both structures.

An additional hypothesis was proposed by Stack and coworkers, who stated that a chiral ligand backbone should force the formation of a helicate and disfavour the formation of a meso-complex.²³ Raymond's group contradicted both hypotheses with an example of both helical and meso complexes assembled by the same chiral ligand. This study went one step further in demostrating that the helicate-to-mesocate interconversion could be driven by the formation of a solvent host–guest complex.²⁴

More recently, Wu *et al.* showed that the encapsulation of anions may be responsible for the anion-dependent formation of helicates *versus* mesocates.²⁵

All of the aforementioned precedents demonstrate that the existing studies concerning the selective discrimination between mesocate/helicate is mainly focused on factors that are directly related to the ligand design.^{26–28} To date, only a few partial studies have shown that different metal ions give rise to different supramolecular structures based on their coordination requirements, as these can have a clear preference for tetrahedral [Cu(1), Ag(1)] or octahedral kernels [Fe(II), Mn(II)].¹ In contrast, a simple methodology based on metal ion recognition that would allow the selective isolation of helicates and mesocates has not yet been systematically investigated.

Thiosemicarbazone ligands are well-known skeletons both in terms of their coordination chemistry and their wide range of biological applications.²⁹ Our research group has pioneered the use of these types of ligands as precursors of different supramolecular arrays. For example, we have reported mesocates, helicates and cluster thiosemicarbazone-derived helicates with unique architectures and promising new functionalities.^{6b,30,31}

We report here the first strategy to achieve synthetic control over the isolation of dinuclear helical or meso-helical complexes by metal-ion recognition. For this purpose we designed a series of five tetradentate bisthiosemicarbazone ligands H_2L^R with different terminal substituents (R = Me, Et, Ph, PhOMe, PhNO₂) (Scheme 1). As the metal ions we chose Co(II), Zn(II) and Cd(II). Our aim was to elucidate the factors that determine the selective formation of helicates and mesocates. These metal ions can give rise to tetrahedral or octahedral kernels by coordination with two or three ligand strands. Electrochemical interaction of these ligands with cobalt, zinc and cadmium plates was carried out and the subsequent formation of helical or meso-helical metallic arrangements was analysed.

Results and discussion

Ligands

The tetradentate ligands H_2L^R (R = Me, Et, Ph, PhN, PhOMe) are composed of two flexible bidentate [NS] domains separated by a rigid aromatic spacer (Scheme 1), thus fulfilling the requirements generally established to assemble helical or meso-helical structures.¹ These ligands were synthesised by the reaction of 1,3-diacetylbenzene and the corresponding thiosemicarbazide precursor, as detailed in the Experimental section. Recrystallisation of the ligand H_2L^{Me} from methanol yielded good quality crystals that were studied by crystallography. Our interest in analysing the structure of this ligand lay in the possibility of predicting the conformational changes required in the ligand to make coordination to two metal centres possible and thus afford helical or meso-helical complexes.

The crystal structure of H_2L^{Me} consists of discrete molecules with the two thiosemicarbazone arms adopting an *anti*-arrangement and an *E* conformation in relation to the two imine bonds (Fig. 1a, Table S1[†]). As expected, this conformation is mainly determined by the existence of both intra- and intermolecular hydrogen bonds (Fig. 1b, Table S2[†]). The imine nitrogen atom and the NH thioamide group of each ligand arm are involved in the intramolecular hydrogen bonds.

Non-classical intramolecular interactions also exist between the aromatic protons H6 and H10 and the imine nitrogen atoms N3 and N4, respectively. Furthermore, the establishment of intermolecular hydrogen bonds between the NH hydrazide group of one ligand arm and the sulfur atom of another neighbouring molecule gives rise to *zig-zag* chains within the crystal cell (Fig. 1b).



Scheme 1 Bisthiosemicarbazone ligands H_2L^R (R = Me, Et, Ph, PhN, PhOMe).



Fig. 1 (a) ORTEP representation of H_2L^{Me} and (b) *zig-zag* chains assembled in the $[H_2L^{Me}]$ crystal cell.

As far as the H_2L^{Me} arrangement is concerned, it must be noted that the donor atoms in one of the bidentate domains (N3/ S1) are oriented in opposite directions. For this reason the coordination of these two donor atoms to the same metal ion would require a conformational rotation in order to make the imine nitrogen and the thioamide sulfur atoms point towards the same metal centre.^{32,33} Furthermore, bearing in mind that the helicate is the minimum energy complex³⁴ and the optimal conformation taken by the free ligand H_2L^{Me} (Fig. 1), the helicate structure should be theoretically more favoured for assemblies of the type [M₂L₂].

Helicate or mesocate assembly

The second step in our study was the preparation of the complexes of the ligands H_2L^R (R = Me, Et, Ph, PhN, PhOMe) with different divalent metal ions, such as Co(II), Zn(II) and Cd(II). It must be noted that Ni(II) and Cu(II) were not included in our study because there is evidence that these two metals induce catalytic hydroxylation of the central arene of the ligand strands,³¹ thus precluding the formation of helical or meso-helical arrangements.

The investigation was initially carried out with Co(II), which has a d⁷ electronic configuration. The coordinative preferences of Co(II) must be considered with care since it is well known that the coordination geometry of the metal depends on the low/high spin state of the metal, which in turn depends on the ligand field strength. Regarding the preferred geometries, cobalt(II) is known to have a four coordinate (tetrahedral) and six coordinate (octahedral) stereochemistry.

Recently, we published the unique structures of the mesocates $[Co_2L_2^{Et}]^{35}$ and $[Co_2L_2^{PhOMe}]$,³⁶ which arise from the electrochemical interaction of a cobalt plate with the ligands H_2L^{Et} and H_2LPh^{OMe} , respectively. Both compounds were previously reported as they were of additional interest beyond their mesocate structure. For example, $[Co_2L_2^{Et}]$ crystallised as an unexpected mixture of linkage and conformational isomers, whereas $[Co_2L_2^{PhOMe}]$ featured a novel type of supramolecular grid structure, a "grid-of-mesocates", in which the grid nodes are simple meso-helical units. These two mesocate compounds are included in this work for comparative purposes.



Fig. 2 ORTEP representation of the mesocate $[Co_2(L^{Me})_2]$ 1.

In order to complete our systematic investigation we performed the electrochemical oxidation of a cobalt plate in a conducting acetonitrile solution of the ligands H_2L^{Me} , H_2L^{Ph} and H_2L^{PhN} . This procedure led to the isolation of the Co(II) com- $[\hat{\mathrm{Co}}_{2}(\mathrm{L}^{\mathrm{Me}})_{2}]\cdot\mathrm{H}_{2}\mathrm{O},$ $[Co_2(L^{Ph})_2]\cdot 2H_2O$ plexes and [Co₂(L^{PhN})₂]·4H₂O. The ESI mass spectra of these complexes contained peaks due to $[Co_2L_2^R + H]^+$. This evidence, together with the analytical data and the conductivity values, led us to propose a neutral [Co₂L₂] stoichiometry for these compounds. The magnetic moments of the Co(II) complexes at room temperature are close to that expected for magnetically diluted Co^{II} ions in a tetrahedral environment (4.2-4.3 B.M.). These complexes were also characterized by IR spectroscopy.

X-ray quality crystals of $[Co_2(L^{Me})_2]$ **1** (Fig. 2, Table S4†) were grown by slow evaporation of the mother liquors from the electrochemical synthesis of compound **5**. In this complex two dianionic strands $[L^{Me}]^{2-}$ are coordinated to two cobalt atoms through an $[N_2S_2]$ donor system that consists of a nitrogen imine atom and a thioamide sulfur atom from one of the ligand arms. This coordination mode gives rise to a *side-by-side* coordination, thus generating a meso-helical structure.

The coordination geometry around the metal ion is distorted tetrahedral, as evidenced by the values of the bond angles between the atoms and the ligand donor system (see Table S5†). The bond distances Co–N and Co–S are in the order of those found in the literature for Co(II) complexes with thiosemicarbazone ligands.³⁷ The intradinuclear Co–Co distances for complexes with R terminal substituents methyl, ethyl and methoxyphenyl are 7.0188(13) Å, 6.7802(20) Å³⁵ and 6.8934(6)³⁶ Å, respectively. Therefore, it appears that the introduction of bulky groups in position 4 of the N terminal branches of the thiosemicarbazone ligands leads to a slight decrease in the intermetallic distances.

Deprotonation of the NH hydrazide groups and coordination to the metal ion through the imine nitrogen and the thioamide sulfur atoms leads to charge delocalization along the ligand. Furthermore, coordination to the cobalt centre gives rise to a conformational change in the thiosemicarbazone arms with respect to the imine bonds. Thus, the configuration changes from E/E in the free ligand to E/Z in the cobalt mesocate $[Co_2(L^{Me})_2]$ **1**.

The crystal lattice of complex **1** reveals the formation of hydrogen bonds between thioamide groups and imine nitrogen atoms of a neighbouring complex molecule (Fig. S6, Table S6[†]).

The Co(II) complexes studied are of additional interest because they are amongst the few examples of cobalt mesocates

described in the literature.^{15*a*,38} More specifically, the only examples reported to date of Co(II) mesocates with bisthiosemicarbazone helicands are compound 1 and the previously reported $[Co_2L_2^{Et}]^{35}$ and $[Co_2L_2^{PhOMe}]$.³⁶

The formation of meso-helicates in all these cases indicates that an increase in the size of the 4-N terminal substituents of the thiosemicarbazone ligands does not affect the type of structure obtained, but it does affect the size and shape of these mesocates.

It was decided to assess a different d^n metal ion with the aim of assessing whether the electronic configuration has any effect on the structure of the assembled complex. Having ruled out Ni(II) and Cu(II) (*vide supra*), we chose the d¹⁰ ion Zn(II), which has a softer acid character compared to Co(II). In addition the ligand-field stabilization energy gain cannot be accomplished by the Zn(II) closed shell d¹⁰ ions. The arrangement of the ligands in the Zn(II) compounds is the result of an equilibrium between the attractive electrostatic metal–ligand forces and the repulsion of the bound residues and this equilibrium may lead to the formation of both octahedral and tetrahedral arrangements.

It should be noted that the structures of the mesocate complexes $[Zn_2(L^{Me})_2]_2$ and $[Zn_2(L^{Et})_2]_2 \cdot 0.5(C_3H_6O)$ were published previously as part of our investigations carried out to establish a successful route to obtain cluster helicates selectively.^{30a} The compounds are included here for comparative purposes.

Oxidation of a zinc plate in the presence of the ligands H_2L^R (R = Ph, PhN, PhOMe) in a conducting acetonitrile solution yielded the complexes $[Zn_2(L^{Ph})_2] \cdot 2H_2O$, $[Zn_2(L^{PhN})_2] \cdot 3H_2O$ and $[Zn_2(L^{PhOMe})_2] \cdot 2H_2O$, respectively. The characterization data for these complexes (ESI, elemental analysis and IR spectroscopy) allow us to propose $[Zn_2L^R_2]$ stoichiometries for these compounds. The ¹H NMR spectra of the zinc complexes do not contain a signal for the hydrazide NH proton, thus confirming the bisdeprotonation of the ligand. In addition, the methyl and phenyl signals show splitting of the terminal NH signal, an observation that may be attributed to the existence of isomers in solution. However, the NMR spectrum of the methoxyphenyl compound contains a single set of resonances. This spectroscopic evidence, together with the poor quality of the nitro complex spectrum, does not provide any valuable information about the structure of these complexes in solution.

Slow evaporation of the acetonitrile mother liquors obtained in the synthesis of $[Zn_2(L^{Et})_2]_2^{30a}$ afforded a different solvent free complex **2**. Recrystallisation of the phenyl and nitrophenyl compounds from chloroform and acetone, respectively, afforded crystals suitable for study by X-ray diffraction. The structures of the complexes were found to be $[Zn_2(L^{Ph})_2] \cdot CH_3 Cl$ **3** and $[Zn_2(L^{PhN})_2]_2 \cdot 5(CH_3)_2 CO$ **4**. Slow evaporation from the methoxyphenyl mother liquors yielded crystals corresponding to $[Zn_2(L^{PhOMe})_2]$ **5** (Table S7†).

The dinuclear zinc complexes 2, 3, 4 and 5 exhibit a box-like achiral meso-helical structure, because the two ligands are *side-by-side* rather than twisted around the zinc(Π) ions (Fig. 3–5). The $[L^R]^{2-}$ bridging ligands act in a fully deprotonated



Fig. 4 ORTEP representation of the mesocates $[Zn_2(L^{Ph})_2]_2$ ·CHCl₃ 3 and $[Zn_2(L^{PhOMe})_2]_2$ ·CHCl₃ 5.



Fig. 3 ORTEP representation of the linkage isomers (a) (top) and (b) (bottom) of mesocate $[Zn_2(L^{Et})_2]_2$ ·2.



Fig. 5 ORTEP representation of the conformational isomers of mesocate $[Zn_2(L^{PhN})_2]_2$ ·5(CH₃)₂CO 4.

bisbidentate fashion and coordinate the zinc(II) ions through the imine nitrogen and the thioamide sulfur atoms. The zinc(II) ions have a distorted tetrahedral four-coordination environment, as evidenced by the bond angles (Tables S8–S10†). The bond distances (Tables S8–S10†) between the metal ion and the kernel donors are in the same order as the values found for Zn(II) complexes derived from thiosemicarbazone ligands.^{30,39} The intermetallic Zn–Zn distances for our complexes with R terminal substituents methyl, ethyl, phenyl, nitrophenyl and methoxyphenyl are 7.1588(11),^{30a} 6.9146(11)^{30a} and 7.0290(8)/7.4407(56), 6.9611(5), 6.8941(12)/6.8030(11) and 5.9262(5) Å, respectively. As in the case of the Co(II) mesocates, functionalisation of the thiosemicarbazone branches with more bulky groups leads to a slight decrease in the metal–metal distances.

Mesocate-type structures have been found on several occasions for zinc complexes with $[N_2O_2]$ ligands^{26b,40} and $[N_4]^{41}$ donors derived from pyridine, pyrazole-phenol or chiral imines, with tetracoordinated metal centres in all cases. However, there are very few examples of zinc mesocates derived from thiosemicarbazone ligands.⁴²

It is worth noting that the asymmetric unit of $[Zn_2(L^{Et})_2]_2 \cdot 2$ contains two linkage isomers (Fig. 3), whereas in the case of mesocate $[Zn_2(L^{PhN})_2]_2 \cdot 5(CH_3)_2CO$ **4** the crystal cell exhibits two conformational isomers (Fig. 5).

The formation of linkage isomers in 2 could be attributed to the fact that [NS] thiosemicarbazone domains can coordinate either the imine or the hydrazide nitrogen atoms and one can therefore consider that these domains can behave in an [(Nim/ Nhy)S] ambidentate manner (Scheme 2). Conformers [Nim/S], a, exhibit behaviour normally observed in thiosemicarbazonate complexes, giving rise to five-membered chelate rings. However, in the linkage isomer [Nhy/S], b, both thiosemicarbazone strands employ different nitrogen atoms for coordination: one of them uses the imine nitrogen atom in a similar manner to the [Nim/S] isomer, but the second domain is bound to the zinc atoms by the hydrazide nitrogen atom instead. This alternative coordination mode is less frequently observed in the coordination chemistry of thiosemicarbazones. The Zn-Zn bond distance is higher in the **b** isomer [7.4407(56) Å] in comparison to the **a** isomer [7.0290(8) Å].

The presence of the two conformers in the unit cell has been found previously^{30a,35} and could be attributed to the need for geometrical optimisation of the hydrogen bond contacts between the conformers. Thus, conformational isomers of complex **4** are connected by hydrogen bonds between the NH thioamide groups and the thioamide sulfur atoms of the neighbouring conformer, as well as with oxygen atoms from solvent molecules. Moreover, there are π - π stacking interactions between the π -cloud of the NO₂ groups and the spacer aromatic rings of a neighbouring conformer, with N–centroid distances of 3.582(7) and 3.625(8) Å



Scheme 2 Ambidentate behaviour of the hydrazide N–N group in a thiosemicarbazone binding domain.

(Fig. 7 and S9[†]). These interactions give rise to an ordered crystal lattice with the acetone molecules trapped inside.

The conformational isomers of **4** arise from the different spatial orientation adopted by one of the terminal nitro phenyl chains in each ligand strand (Fig. 6). The different arrangement of these conformers is clearly shown by the values of the S–Zn–S bond angles (see Table S6,† Fig. 6), as well as by the different chelate ring angles (84.60° in isomer a, 77.20° in isomer b). The Zn–Zn intermetallic distance is very similar in the two conformers (*vide supra*).

The crystal cell of the complexes **3** and **5** reveals the establishment of hydrogen bonds between the sulfur atoms and the NH thioamide groups of a neighbouring complex (Table S7†), a situation that gives rise to the growth of chains in the crystal lattice. In addition, in complex **3** π – π stacking interactions occur between the aromatic rings of the spacer (*centroid–centroid* distance 3.778(2) Å, Fig. S7†).

As mentioned before for the Co(II) mesocates, the Zn(II) analogues also have a Z/E configuration of the thiosemicarbazone branches with respect to the imine bonds, thus confirming the need for conformational rotation to achieve meso-helical arrangements. The meso-helical structures achieved with Zn(II) ions also demonstrate that a change from Co(II) to a similar-sized metal ion like Zn(II), which lacks ligand-field stabilization energy, does not influence the arrangement of the bisthiosemicarbazone ligands around the two metal ions. Besides, a change in the size and nature of the 4-N terminal substituents of the thiosemicarbazone ligands does not have any effect on the type of structure obtained (mesocates) but it does influence the compacticity of the meso-helical molecules.

The next step in our investigation was to study another metalrelated factor that may be involved in the assembly process, *i.e.* the size of the metal ion. Thus, keeping the d^{10} closed-shell nature, we chose the larger metal ion Cd(II). Cd(II) can be also found in tetrahedral and octahedral arrangements and a preferred coordination kernel cannot be defined.



Fig. 6 Overlapped coordination kernels for the conformational isomers of mesocate 4.



Fig. 7 Non-covalent interactions between conformational isomers of mesocate $[Zn_2(L^{PhN})_2]_2$:5(CH₃)₂CO 4.

Recently we reported the cadmium helicate $[Cd_2(L^{Ph})_2]_2$, which assembles into chains of enantiomers in the solid state,⁴ and [Cd₂(L^{Me})₂]₂·DMSO, which forms a novel supramolecular topology that we named "grid-of-helicates" with the DMSO molecule acting as a superglue agent.⁴⁴ In order to provide further support for these results we performed the electrochemical oxidation of a cadmium plate in the presence of acetonitrile solutions of ligands H_2L^R (R = Et, PhN, PhOMe). These syntheses gave rise to the complexes $[Cd_2(L^{Et})_2] \cdot H_2O$, $[Cd_2(L^{PhN})_2] \cdot 3H_2O$ and $[Cd_2(L^{PhOMe})_2]$, respectively. The ESI mass spectra of these complexes are consistent with the formation of dinuclear species since peaks due to $[M_2L_2 + H]^+$ were identified. The elemental analysis data and the conductivity values confirm the neutral and dinuclear nature of all these complexes. The ¹H NMR spectra of the cadmium complexes are also indicative of the dianionic character of the ligand in the complexes, but do not provide further information about their structure in DMSO solutions, as was the case for the previously discussed zinc derivatives.

The Cd(π) complexes were also characterized by means of ¹¹³Cd NMR studies (Fig. S5†). Thus, the ¹¹³Cd NMR spectra exhibit signals at 559.0 and 542.4 ppm for ethyl and methoxy-phenyl complexes, respectively, and these values are close to those found for Cd(π) complexes with [N₂S₂] coordination environments in DMSO solutions. The positions of these signals indicate that the tetracoordinated kernel found in the solid state (*vide infra*) is retained in solution.⁴⁵ In the case of the nitrophenyl complex, the signal appears at 454.4 ppm (Fig. S1†) and this is indicative of the coordination of a DMSO solvent molecule to the Cd(π) ions in solution, thus making the compound an unsaturated helicate.

Recrystallisation of the nitrophenyl complex from acetone yielded crystals suitable for X-ray diffraction studies. Analysis of the structural data revealed a helical structure of formula $[Cd_2(L^{PhN})_2]$ ·4(CH₃)₂SO **6** (Table S7†) (Fig. 7). The helicate is constructed by two bideprotonated ligand units $(L^{PhN})^{2-}$ arranged in a helical mode around two cadmium(π) metal ions (Fig. 8). The two enantiomers (*P* and *M*) alternate through the crystal cell. The dihelicate **6** is additionally solvated by four DMSO molecules.

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 confirmed by the values of the metal-donor set bond angles (Table S13†). This distortion is higher than that exhibited by the meso-helical arrangements in the cases of cobalt(II) and zinc(II) ions. The



Fig. 8 ORTEP diagram of the dihelicate 6.

bond distances Cd–N and Cd–S in **6** are in the order of those found in the literature for Cd(II) complexes derived from thiosemicarbazone ligands.^{37b,43,46} The intrahelicate Cd–Cd distances are 5.2911(3), 5.2492(3) and 5.0178(4) Å for complexes with terminal substituents methyl, phenyl and nitrophenyl, respectively. As expected, helicates have more compact structures than mesocates. Furthermore, in a similar way to the Co(II) and Zn(II) mesocates, functionalisation of the thiosemicarbazone branches with more bulky groups leads to a slight decrease in the metal– metal distances.

As demonstrated previously for the analogue $[Cd_2(L^{Ph})_2]_2$, helicate **6** exhibits π – π stacking interactions between the nitrophenyl terminal groups of neighbouring molecules, thus giving rise to parallel infinite chains of helicate diastereoisomers. This packing mode differs from that found in the previously reported $[Cd_2(L^{Ph})_2]_2$, in which dihelical enantiomer pairs assembled into an infinite linear chain.⁴³ Both cases are clear examples of hierarchical self-assembly because discrete dihelicate complexes aggregate in a second supramolecular approach (Fig. 9).^{11a,47} This result also confirms that the presence of an aromatic ring at each of the four ends of the dihelicate favours aggregation into 1D chains through π -stacking interactions, whereas functionalisation of the supramolecule with alkyl groups leads to the assembly of hydrogen-bonded 1D chains or unsaturated grid-ofhelicates instead.

The X-ray diffraction studies carried out on the Co(II) and Zn(II) mesocates **1–5** and the Cd(II) dihelicate **6** showed significant differences in terms of the conformation of the ligand arms. Thus, the configuration adopted by the ligand with respect to the imine bonds when they are bound to Co(II) and Zn(II) ions in meso-helical structures is E/Z (or pseudo-C), whereas for the Cd(II) helicates an E/E configuration (also called pseudo-S) is observed (Fig. 10). This fact implies that dihelicate formation requires fewer conformational rotations and is therefore the thermodynamically most stable metal structure. Moreover, the Cd(II) helicates prove that an increase in the degree of hindrance in the ligand by functionalisation of the terminal NH thioamide group does not affect the type of supramolecular structure assembled but it does affect the crystal packing mode (1D chains or grid-of-helicates).



Fig. 9 Aggregation of 6 by π -stacking interactions into infinite chains of diastereoisomers.



Fig. 10 Representation of the naked ligand $[L^{PhN}]^{2-}$ in (a) mesocate 4 and (b) helicate 6.

Bearing in mind that the increase in radius of first-row transition metal cations through the series is not large [72 pm for Co(II) and 74 pm for Zn(II) in four-coordinated tetrahedral environments], a similar behaviour is expected for the ligand when it coordinates to Co(II) and Zn(II) ions. The formation of meso-helical structures for Co(II) and Zn(II) ions but the formation of helicates for Cd(II) confirms this prediction.

In the cases of Zn(II) mesocates and Cd(II) helicates, both metal ions have the same d^{10} electronic configuration and this does not provide crystal stabilization – although they do differ in their ionic radius [92 pm for Cd(II) in a four-coordinated tetrahedral environment]. This size increase may explain the fact that the ligand strands are helically arranged around the two cadmium atoms in order to satisfy their tetrahedral coordinative requirements.

All of the results obtained for the series of complexes constructed with the H_2L^R thiosemicarbazone ligands and the selected metal ions Co(II), Zn(II) and Cd(II) by means of electrochemical synthesis are summarised above. The data obtained clearly indicate that we can selectively control the isolation of helicate or mesocate compounds by metal self-assembly recognition.

Conclusions

The coordination of [NS] bisbidentate ligands to different metal ions has allowed us to obtain mesocate or dihelicate complexes by direct metal-ion recognition: meso-helical compounds are formed in the cases of Co(II) and Zn(II) whereas Cd(II) ions give rise to double helicates. The size of the metal ion seems to be the key factor that determines the conformational change of the ligand upon metal coordination and therefore the formation of mesocates or helicates.

Experimental

Materials

All solvents, 1,3-diacetylbenzene, 4-methoxyphenyl-isothiocyanate, hydrazine monohydrate, 4-N-R-3-thiosemicarbazides (R = Me, Ph, PhNO₂) and tetraethylammonium perchlorate are commercially available and were used without further purification. Metals (Aldrich) were used as $ca. 2 \times 2 \text{ cm}^2$ plates.

Physical measurements

Elemental analyses (C, H and N) were performed on a Carlo Erba EA 1108 analyser. ¹H NMR spectra were recorded on Bruker DPX-250 and Varian Inova 500 spectrometers using DMSO- d_6 as a solvent. ¹¹³Cd NMR spectra were recorded on a Bruker AMX-500 spectrometer using DMSO-d₆ as a solvent. Chemical shifts are expressed relative to tetramethylsilane (¹H NMR) and 0.1 M Cd(ClO₄)₂ (¹¹³Cd NMR) as external references. Infrared spectra were measured on KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1} . Electrospray ionization (ESI) mass spectra were registered on an API4000 Applied Biosystems mass spectrometer. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were registered on a Bruker Autoflex spectrometer using DCTB as the matrix. Molar conductivity values were obtained at 25 °C from a 10^{-3} M solution in acetone on a Crison micro CM 2200. Room temperature magnetic susceptibility was measured using a Digital Measurement system MSB-MKI, calibrated using mercury tetrakis(isothiocyanato)cobalt(II).

Ligand synthesis

 H_2L^{Me} . The synthesis and characterization of the ligand bis(4-*N*-methylthiosemicarbazone)-1,3-diacetylbenzene were previously reported by us.^{30*a*} Recrystallisation from methanol of the isolated solid yielded crystals of $[H_2L^{Me}]$ and these were studied by X-ray diffraction.

 H_2L^{Et} . The synthesis and characterization of the ligand bis(4-*N*-ethylthiosemicarbazone)-1,3-diacetylbenzene, H_2L^{Et} , were previously reported by our group.^{30a}

H₂L^{Ph}. The ligand bis(4-N-phenylthiosemicarbazone)-1,3-diacetylbenzene, H₂L^{Ph}, was prepared by condensation of 1,3-diacetylbenzene (0.73 g, 4.5 mmol) with 4-N-phenyl-3thiosemicarbazide (1.11 g, 9 mmol) in ethanol (125 mL). The solution was heated under reflux for 10 h and concentrated with a Dean-Stark trap to ca. 20 mL (Scheme S1[†]). The pale yellow precipitate was collected by filtration. The resulting solid was finally washed with diethyl ether $(3 \times 10 \text{ mL})$ and dried in vacuo. Yield: 1.23 g, 82%. Anal. C26H28N6S2O2 requires: C, 60.0; H, 5.0; N, 16.1; S, 12.3. Found: C, 59.9; H, 5.1; N, 16.0; S, 12.1. MS ESI (m/z) 519.2 $[H_2L - H]^-$; IR (KBr, cm⁻¹): v(NH) 3307 (w), 3242 (w), v(C=N + C-N) 1595 (w), 1544 (s), 1521 (s), 1477 (m), v(C=S) 1111 (m), 800 (w), v(N-N) 1030 (m); ¹H NMR $\delta_{\rm H}$ (DMSO-d₆, ppm): 10.53 (s, 2H), 10.01 (s, 2H), 8.38 (s, 1H), 8.03 (d, 2H, J = 7.7 Hz), 7.44 (t, 1H, J = 7.7 Hz), 7.34 (d, 4H, J = 8.8 Hz), 6.90 (d, J = 8.8 Hz), 3.77 (s, 6H), 2.42 (s, 6H).

 H_2L^{PhN} . The ligand bis(4-*N*-(4-nitrophenyl)thiosemicarbazone)-1,3-diacetylbenzene, H_2L^{PhN} , was prepared by condensation of 1,3-diacetylbenzene (0.73 g, 4.5 mmol) with 4-*N*-(4-nitrophenyl)-3-thiosemicarbazide (1.28 g, 9 mmol) in ethanol

(125 mL). The solution was heated under reflux for 10 h and concentrated with a Dean–Stark trap to *ca.* 20 mL (Scheme 1). The yellow precipitate was collected by filtration. The resulting solid was washed with diethyl ether (3 × 10 mL) and dried *in vacuo.* Yield: 1.21 g, 81%. Anal. $C_{24}H_{22}N_8O_4S_2$ requires: C, 52.4; H, 4.0; N, 20.4; S, 11.9%. Found: C, 51.8; H, 4.1; N, 20.5; S, 11.8; MS ESI (*m/z*): 549.1 [H₂L – H]⁻; IR (KBr, cm⁻¹): v(NH) 3283 (w), 3198 (w), 3263 (m), v(C=N + C-N) 1597 (w), 1546 (s), 1477 (m), v(C=S) 1113 (m), 852 (m), v(N-N) 1059 (w), $v(NO_2)$ 1504 (m), 1334 (s). ¹H NMR δ_{H} (DMSO-d₆, ppm): 11.05 (s, 2H), 10.43 (s, 2H), 8.40 (s, 1H), 8.15 (d, 4H, *J* = 9.0 Hz), 8.06 (d, 2H, *J* = 7.8 Hz), 7.98 (d, 4H, *J* = 9.0 Hz), 7.50 (t, 1H, *J* = 7.8 Hz), 2.46 (s, 6H).

Precursor 4-*N***-(4-methoxyphenyl)-3-thiosemicarbazide H**₂**PhOMe.** Hydrazine monohydrate (1.48 g, 30 mmol) was slowly added to a solution of 4-methoxyphenyl-isothiocyanate (2.47 g, 15 mmol) in 20 mL of absolute ethanol with stirring at 0 °C (Scheme S2†). After 1 h the white solid was filtered off, washed with diethyl ether and dried under vacuum. Yield: 2.55 g (85%). Anal. C₈H₁₁N₃SO requires: C, 48.7; H, 5.6; N, 21.3; S, 16.2. Found: C, 48.6; H, 5.6; N, 21.3; S, 16.2. MS ESI (*m/z*) 196.1 [H₂PhOMe – H]⁻; IR (KBr, cm⁻¹): *v*(NH) 3321 (m), 3275 (w), 3167 (m), *v*(C=N + C–N) 1529 (vs), 1512 (s), 1491 (m), *v*(C=S) 1105 (w), 833 (w), *v*(N–N) 1034 (m); ¹H NMR δ_H(DMSO-d₆, ppm): 9.51 (s, 1H), 8.97 (s, 1H), 7.42 (s, 2H, *J* = 8.4 Hz), 6.84 (d, 2H, *J* = 8.4 Hz), 4.72 (s, 2H), 3.73 (s, 3H).

 H_2L^{PhOMe} . The thiosemicarbazone ligand H_2L^{PhOMe} was obtained by condensation of the previously synthesised 4-N-(4methoxyphenyl)-3-thiosemicarbazide (1.12 g, 9 mmol) with 1,3diacetylbenzene (0.73 g, 4.5 mmol) (Scheme S1⁺). For this reaction both reactants were ground in an agate mortar until a homogeneous mixture was obtained. The mixture was introduced into a vial and was sonicated for 6 h. The resulting yellow oil was triturated with 20 mL of absolute ethanol to give a white solid, which was filtered off, washed with diethyl ether and dried under vacuum. Yield: 1.27 g, 85%. Anal. C₂₆H₂₈N₆S₂O₂ requires: C, 60.0; H, 5.0; N, 16.1; S, 12.3. Found: C, 59.9; H, 5.1; N, 16.0; S, 12.1. MS ESI (*m/z*) 519.2 [H₂L - H]⁻; IR (KBr, cm⁻¹): v(NH) 3307 (w), 3242 (w), v(C=N + C-N) 1595 (w). 1544 (s), 1521 (s), 1477 (m), v(C=S) 1111 (m), 800 (w), v(N-N) 1030 (m); ¹H NMR δ_{H} (DMSO-d₆, ppm): 10.53 (s, 2H), 10.01 (s, 2H), 8.38 (s, 1H), 8.03 (d, 2H, J = 7.7 Hz), 7.44 (t, 1H, J = 7.7 Hz), 7.34 (d, 4H, J = 8.8 Hz), 6.90 (d, J = 8.8 Hz), 3.77 (s, 6H), 2.42 (s, 6H).

Synthesis of the complexes. The metal complexes were obtained using an electrochemical procedure.⁴⁸ As an example the synthesis of $[Co_2(L^{Me})_2]$ ·H₂O is described below.

 $[Co_2(L^{Me})_2]$ ·H₂O. An acetonitrile solution of the ligand containing about 10 mg of tetraethylammonium perchlorate as the supporting electrolyte was electrolyzed using a platinum wire as the cathode and a metal plate as the anode. The cell can be summarised as: Pt(-)|H₂L^R + MeCN|Co(+). A solution (0.1 g, 0.19 mmol) of the ligand in acetonitrile (80 mL), containing 10 mg of tetraethylammonium perchlorate (CAUTION: although problems were not encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care), was electrolyzed for 62 min using a current of 10 mA. The resulting green solid was filtered off, washed with diethyl ether and dried *in vacuo*.

[Co₂(L^{Me})₂]·H₂O. Yield: 0.13 g, 95%. Anal. Co₂C₂₈H₃₈N₁₂S₄O requires: C, 49.4; H, 4.1; N, 18.2; S, 13.9. Found: C, 48.9; H, 4.2; N, 18.1; S, 14.0. MS ESI (*m*/*z*) 394.2 [ML + H]⁺, 730.0 [ML₂ + H]⁺, 787.0 [M₂L₂ + H]⁺; IR (KBr, cm⁻¹): *v*(OH) 3426 (w), *v*(NH) 3369 (w), *v*(C=N + C–N) 1589 (w), 1547 (w), 1491 (s), *v*(C=S) 1097 (w), 797 (w), *v*(N–N) 1049 (w); $\Lambda_{\rm M}$ (µS cm²) = 17.5; µ (B.M.) = 4.2. Slow evaporation of the mother liquors gave crystals of complex [Co₂(L^{Me})₂] **1** that were suitable for X-ray diffraction studies.

The synthesis and structure of $[Co_2(L^{Et})_2]^{35}$ and $[Co_2(L-Ph^{OMe})_2]^{36}$ were previously reported by us.

[Co₂(L^{Ph})₂]·2H₂O. Yield: 0.11 g, 78%. Anal. Co₂C₄₈H₄₈N₁₂S₄O₂ requires: C, 53.8; H, 4.5; N, 15.7; S, 12.0. Found: C, 53.9; H, 4.2; N, 16.2; S, 12.0. MS ESI (*m*/*z*) 518.0 [ML + H]⁺, 979.3 [ML₂ + H]⁺, 1035.1 [M₂L₂ + H]⁺; IR (KBr, cm⁻¹): ν (OH) 3402 (w), ν (NH) 3305 (w), ν (C=N + C–N) 1599 (m), 1530 (s), 1494 (s), ν (C=S) 1113 (w), 752 (w), ν (N–N) 1055 (w); $\Lambda_{\rm M}$ (μ S cm²) = 12.3; μ (B.M.) = 4.2.

 $[Co_2(L^{PhN})_2]$ ·4H₂O. Yield: 0.10 g, 82%. Anal. $Co_2C_{48}H_{50}$ -N₁₆S₄O₁₃ requires: C, 42.4; H, 4.1; N, 16.5; S, 9.4. Found: C, 42.3; H, 3.8; N, 16.4; S, 8.8. MS ESI 609.1 [ML + H]⁺, MAL-DI-TOF (*m*/*z*) 608.1 [ML + H]⁺, 668.6 [M₂L + H]⁺, 1215.1 [M₂L₂]⁺; IR (KBr, cm⁻¹): *v*(OH) 3417 (w), *v*(NH) 3303 (w), *v*(C=N + C–N) 1597 (m), 1546 (m), 1497 (s), 1479 (s), *v*(NO₂) 1329 (s), *v*(C=S) 1113 (m), 851 (w), *v*(N–N) 1057 (w); Λ_M (µS cm²) = 10.1; µ (B.M.) = 4.3.

The crystal structures of $[Zn_2(L^{Me})_2]$ and $[Zn_2(L^{Et})_2] \cdot 0.5$ (C₃H₆O) were published previously.^{30*a*} Recrystallisation of the $[Zn_2(L^{Et})_2]$ acetonitrile mother liquors afforded crystals corresponding to the different solvent free structure **2**.

[Zn₂(L^{Ph})₂]·2H₂O. Yield: 69%. 0.09 g, Anal. Zn₂C₄₈H₄₄N₁₂S₄O₂ requires: C, 53.4; H, 4.1; N, 15.6; S, 11.9. Found: C, 53.2; H, 4.1; N, 15.2; S, 11.6. MS ESI (m/z) 520.2 $[ML + H]^+$, 587.3 $[M_2L + H]^+$, 1041.3 $[M_2L_2 + H]^+$; ¹H NMR $\delta_{\rm H}$ (DMSO-d₆, ppm): 9.45 (s, 1H), 9.01 (s, 1H), 8.57 (s, 1H), 7.75 (d, 4H, J = 7.7 Hz), 7.61 (t, 1H, J = 6.6 Hz), 7.38 (d, 2H, J = 8.4 Hz), 7.31 (t, 1H, J = 8.4 Hz), 6.98 (m, 4H, J = 7.7, 6.6 Hz), 6.86 (t, 1H, J = 6.6 Hz), 2.78 (s, 3H), 2.34 (s, 3H); IR (KBr, cm⁻¹): v(OH) 3395 (w), v(NH) 3312 (w), v(C=N + C-N) 1597 (w), 1529 (s), 1493 (s), v(C=S) 1120 (m), 753 (w), v(N-N) 1032 (w); Λ_M (μ S cm²) = 11.7. Recrystallisation of [Zn₂(L^{Ph})₂]·2H₂O from CHCl₃ led to the isolation of yellow crystals of [Zn₂(L^{Ph})₂]·2CHCl₃ 3.

[**Zn₂(L₂^{PhN})₂]·3H₂O.** Yield: 0.09 g, 73%. Anal. Zn₂C₄₈H₄₆-N₁₆S₄O₁₁ requires: C, 43.1; H, 3.9; N, 16.8; S, 9.6. Found: C, 43.3; H, 3.5; N, 17.0; S, 9.9. MS ESI (*m*/*z*) 636.9 [ML + Na]⁺, 680 [M₂L + H]⁺; MS MALDI-TOF (*m*/*z*) 613.1 [ML]⁺; ¹H NMR δ_H(DMSO-d₆, ppm): 10.06 (s, 1H), 9.95 (s, 2H), 8.18 (m, 4H + 4H), 8.05 (m, 1H), 8.03 (m, 1H), 7.87 (m, 1H), 2.34 (s, 6H); IR (KBr, cm⁻¹): *v*(OH) 3402 (sh), *v*(NH) 3364 (w), 3290 (w), *v*(C=N + C-N) 1597 (m), 1547 (m), 1495 (s), 1475 (s), *v*(NO₂) 1329 (s), *v*(C=S) 1113 (m), 851 (w), *v*(N–N) 1067 (w); A_{M} (μS cm²) = 9.3. Recrystallisation of [Zn₂(L^{PhN})₂]·3H₂O from acetone led to the isolation crystals of the complex $[Zn_2(L^{PhN})_2]_2{\cdot}5(CH_3)_2CO$ 4 and these were characterized by X-ray diffraction.

[**Zn**₂(**L**^{PhOMe})₂]·**2H**₂**O**. Yield: 0.10 g, 76%. Anal. Zn₂C₅₂H₅₆-N₁₂S₄O₆ requires: C, 51.9; H, 4.7; N, 14.0; S, 10.7. Found: C, 51.6; H, 4.5; N, 14.3; S, 10.4. MS ESI (*m/z*) 583.1 [ML + H]⁺, 650.3 [M₂L + H]⁺, 1103.3 [ML₂ + H]⁺; MS MALDI-TOF (*m/z*) 583.2 [ML]⁺, 1169.4 [M₂L₂ + H]⁺; ¹H NMR δ_H(DMSO-d₆, ppm): 8.95 (s, 2H), 8.41 (s, 1H), 7.68 (d, 2H, *J* = 7.7 Hz), 7.59 (d, 4H, *J* = 8.8 Hz), 7.41 (m, 1H, *J* = 7.7 Hz), 6.82 (d, 4H, *J* = 8.8 Hz), 3.76 (s, 6H), 2.26 (s, 6H); IR (KBr, cm⁻¹): *v*(OH) 3436 (w), *v*(NH) 3397 (m), *v*(C=N + C-N) 1593 (w), 1509 (s), 1474 (s), *v*(C=S) 1100 (w), 797 (w), *v*(N–N) 1034 (m); *A*_M (µS cm²) = 5.7. Slow evaporation of the mother liquors of [*Zn*₂(L^{PhOMe})₂]·*2H*₂O yielded the new crystalline complex [Zn₂(L^{PhOMe})₂] **5**, which was characterized by X-ray diffraction.

The synthesis and full characterization of $[Cd_2(L^{Ph})_2]$ and $[Cd_2(L^{Ph})_2]$ have recently been reported by us.^{43,44}

[Cd₂(L^{Et})₂]·H₂O. Yield: 0.12 g, 82%. Anal. Cd₂C₃₂-H₄₆N₁₂S₄O₁ requires: C, 39.7; H, 4.8; N, 17.4; S, 13.3. Found: C, 39.7; H, 4.8; N, 17.4; S, 13.3. MS ESI (*m*/*z*) 476.9 [ML + H]⁺, 589.4 [M₂L + H]⁺, 948.0 [M₂L₂ + H]⁺; ¹H NMR δ_H(DMSO-d₆): 8.34 (s, 1H_A), 7.73 (d, 1H_B, *J* = 7.4 Hz), 7.57 (d, 2H_A, *J* = 7.6 Hz), 7.48 (dd, 1H_B, *J*₁ = 8.2 Hz, *J*₂ = 6.9 Hz), 7.37 (s broad, 1H_B), 7.20 (t, 1H_B, *J* = 7.6 Hz), 6.98 (t, 1H_B, *J* = 6.2 Hz), 6.84 (t, 1H_B, *J* = 4.9 Hz), 6.73 (t, 2H_A, *J* = 4.6 Hz), 3.40 (m, 4H_A), 3.18 (m, 4H_B), 2.43 (s, 6H_A), 1.79 (s, 6H_B), 1.16 (t, 6H_A, *J* = 6.9 Hz), 1.08 (t, 6H_B, *J* = 6.9 Hz) ppm. IR (KBr, cm⁻¹): *v*(OH) 3420 (w), *v*(NH) 3348, 3327 (w), *v*(C=N + C–N) 1566 (m), 1515 (m), *v*(C=S) 1091 (m), 846 (w), *v*(N–N) 1057 (w); Λ_M (μS cm²) = 4.0.

[Cd₂(L^{PhN})₂]·3H₂O. Yield: 0.12 g, 82%. Anal. Cd₂C₄₈H₄₆-N₁₆S₄O₁₁ requires: C, 41.9; H, 3.4; N, 16.3; S, 9.3. Found: C, 41.5; H, 3.3; N, 16.0; S, 8.9. MALDI-TOF (*m*/*z*) 663.1 [ML + H]⁺, 773.5 [M₂L + H]⁺; ¹H NMR δ_H(DMSO-d₆): 9.66 (s, 2H, H₂), 8.64 (s, 1H, H₃), 7.94 (d, 4H, H₄ + 4H, H₆), 7.70 (m, 2H, H₅), 7.56 (m, 1H, H₇), 2.33 (s, 6H, H₈); ¹¹³Cd NMR (DMSO-d₆): δ 454.4 ppm; IR (KBr, cm⁻¹): *v*(OH) 3405 (w), *v*(NH) 3367 (w), *v*(C=N + C–N) 1597 (m), 1544 (m), 1495 (s), 1472 (s), *v*(NO₂) 1328 (s), *v*(C=S) 1113 (m), 848 (w), *v*(N–N) 1062 (w); $\Lambda_{\rm M}$ (µS cm²) = 8.3. Recrystallisation from acetone yielded crystals of [Cd₂(L^{PhN})₂]·4(CH₃)₂SO **6** that were suitable for X-ray diffraction.

[Cd₂(L^{PhOMe})₂]. Yield: 0.11 g, 78%. Anal. Cd₂C₅₂H₅₂-N₁₂S₄O₄ requires: C, 49.5; H, 4.2; N, 13.3; S, 10.2. Found: C, 49.0; H, 4.1; N, 13.0; S, 9.9. MS ESI (*m*/*z*) 633.1 [ML + H]⁺, 1153.2 [ML₂ + H]⁺; MS MALDI-TOF (*m*/*z*) 1263.1 [M₂L₂ + H]; ¹H NMR $\delta_{\rm H}$ (DMSO-d₆): 8.84 (s, 2H, H₂), 8.48 (s, 1H, H₃), 7.66 (d, 2H, H₄, *J* = 7.7 Hz), 7.62 (d, 4H, H₆, *J* = 8.8 Hz), 7.55 (t, 1H, H₅, *J* = 7.7 Hz), 6.75 (d, 4H, H₇, *J* = 8.8 Hz), 3.75 (s, 6H, H₈), 2.28 (s, 6H, H₉); ¹¹³Cd NMR (DMSO-d₆): δ 542.4 ppm; IR (KBr, cm⁻¹): *v*(NH) 3397 (w), *v*(C=N + C–N) 1591 (w), 1509 (s), 1474 (s), *v*(C=S) 1113 (w), 797 (w), *v*(N–N) 1034 (w); $\Lambda_{\rm M}$ (µS cm²) = 4.1.

X-ray crystallography

Data for H₂L^{Me}, 2, 3, 4, 5 and 6 were collected on a Bruker APPEX 2 diffractometer and data for 1 were collected on a Bruker SMART 1000 diffractometer, all using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube source (at 100 K). The computations and reduction were carried out with APEX2. In all cases an empirical absorption correction was applied using SADABS.⁴⁹ All of the structures were solved by SIR- 97^{50} except for 3, which was solved by SIR2004⁵¹ and all were refined by full-matrix least-squares techniques against F^2 using SHELXL-97.⁵² Positional and anisotropic atomic displacement parameters were refined for all heteroatoms. The hydrogen atom positions were included in the model by electronic density and refined isotropically $[U_{iso}(H) =$ $1.2U_{eq}(atom)$] or were geometrically calculated and refined using a riding model (isotropic thermal parameters 1.2-1.5 times those of their carrier atoms). Criteria for a satisfactory complete analysis were the ratios of "rms" shift to standard deviation of less than 0.001 and no significant features in the final difference maps. Molecular graphics were obtained with ORTEP.53 A summary of the crystal data, experimental details and refinement results is given in Tables S1, S4, S7 and S12.⁺ Significant bond distances and angles are summarized in Tables S3, S5, S8, S9, S10 and S13,[†] while hydrogen bond parameters are shown in Tables S2, S6, S11 and S14.[†]

CCDC 893868–893874 contain the supplementary crystallographic data for this paper.

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