Thermodynamically controlled products: novel motif of metallohelicates stabilized by inter- and intra-helix hydrogen bonds

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Two temperature and/or time dependent self-assembly processes of maleic dianion (male), thiourea and zinc(II) or cadmium(II) ions have been studied. By prolonging the reaction time and heating, the kinetic product $[\{Zn(male)(tu)(H_2O)\}_2]\cdot 4H_2O$ **1** can be converted into the thermodynamic product $[\{Zn(male)(tu)_2\}_n]$ **2**. In the case of the Cd–maleate–tu system, the thermodynamic product with helical formation $[\{(male)Cd(tu)_2\}_2(male)\text{-}Cd(tu)(H_2O)_2]_n$ **4** was obtained from the kinetically controlled product $[Cd(Hmale)_2(tu)_2(H_2O)_2]$ **3** by prolonging the reaction time. The thermodynamic helicate **2** bears a new metallohelicate motif in which the helical structure is induced and stabilized by interhelix hydrogen bonding. On the contrary, **4** also bears an infinite metallohelicate motif where the helix is induced and stabilized by intrahelix hydrogen bonding and a 3-D network is formed through hydrogen bonds and short S · · · S contacts among neighboring helixes. All the complexes were characterized by X-ray crystallography.

Introduction

The use of metal ions to control the self-assembly of discrete supramolecular species has been an area of intense interest in recent years, in particular that of complexes presenting a helical arrangement of ligand strands.[1–3] This interest has been driven, at least in part, by the potential use of helicates as functional components of molecular devices.[2] In the past decade many wondrous examples of metallohelicates have been described.[3–5] However, the most relevant parameters of previous strategies for controlling the architecture are the molecular size, topology, stereochemistry, and shape. Helixes are constructed by taking advantage of the co-ordination preference of the chosen metal and the geometrical preference of the chosen ligand.[3d,4f–h,5b,6,7] Here, we present novel helical motifs in which the infinite single metallohelicates were constructed by inter- or intra-helix hydrogen bonds. In fact, using hydrogen bonds to assemble supramolecular array has widely been studied.[8] However, direct self-assembly of infinite helixes by multiple components (three or four) is still rare. It is known that, in the self-assembly of both synthetic and biological systems, the thermodynamic product is usually formed; kinetic products may also be obtained if the shape of the energy hypersurface is such that the system becomes trapped in local minima.[9] In fact, the self-assembly of both the present complexes **2** and **4** is evidently a temperature and time dependent process; these thermodynamic products are formed from kinetic products **1** and **3**.

Results and discussion

Synthesis and structure of $[\{Zn(male)(tu)(H_2O)\}_2]\cdot 4H_2O$ 1 and $[\{Zn(male)(tu)_2\}_n]$ 2

X-Ray analyses reveal that complex **1** possesses a binuclear macrocycle structure (Fig. 1) and **2** a infinite single helical structure (Figs. 3 and 4). It is interesting that **1** and **2** self-assemble from the same solution. The self-assembly of the maleic acid,
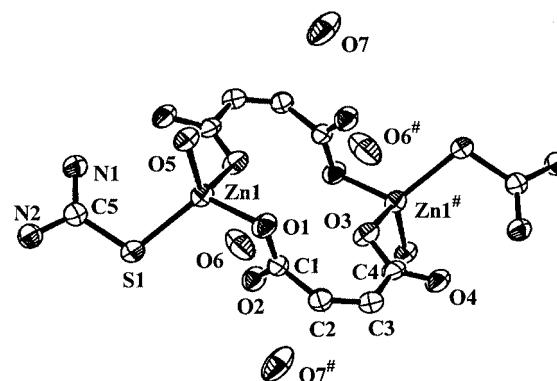

Fig. 1 Crystal structure of binuclear macrocycle **1** (#: $1 - x$, $1 - y$, $1 - z$).

thiourea and zinc(II) ion yields the binuclear macrocycle structure **1** after a relative short reaction time at room temperature, whereas the helicate **2** is obtained after a prolonged reaction time or heating. At high temperature the second co-ordinated water molecule in **1** is replaced by thiourea, eqn. (1), inducing

$$\text{Binuclear cycle } \mathbf{1} + \text{tu} \xrightarrow{\text{heat}} \text{Helix } \mathbf{2} \qquad (1)$$
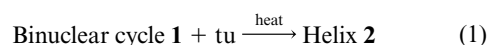
formation of anhydrous **2**. The present results indicate that the binuclear macrocycle **1** is a kinetic product, formed reversibly from the components, which progressively converts into the thermodynamic product, the helicate **2**. The higher stability of **2** might be attributed to several factors, such as a hydrogen-bonded 3-D framework, or strain in the bound ligand and/or at the co-ordination centers, and also the enthalpic contribution.

In the structure **1**, two zinc(II) ions are connected by two maleic dianions to form a macrocycle, see Fig. 1. The zinc ions are tetrahedrally co-ordinated by two carboxyl atoms, one water molecule and one thiourea molecule. Four water
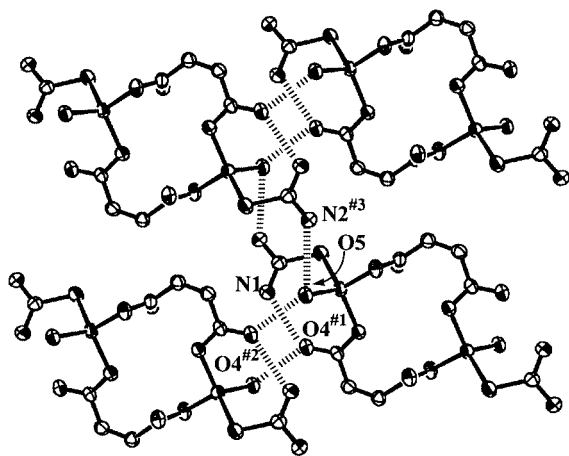
A
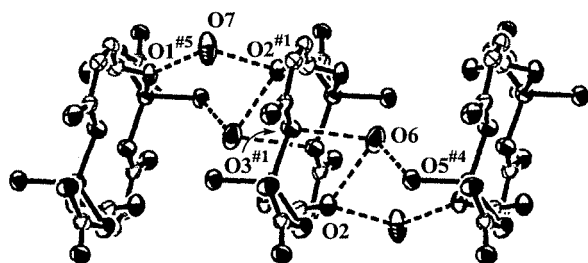
B

Fig. 2 Hydrogen bonded network of complex **1**. **A**: 2-D layer structure linked by intermolecular hydrogen bonds. Hydrogen bond lengths (Å): N1···O4#1, 2.855; O5···O4#2, 2.699; O5···N2#3, 3.073. #1: $1 - x$, $1 - y$, $1 - z$; #2: x, $y - 1$, $z - 1$. #3: $1 - x$, $1 - y$, $2 - z$. **B**: Water molecules filling the space between layers and involved in hydrogen bonds. Hydrogen bond lengths (Å): O6···O5#4, 2.640; O6···O3#1, 2.995; O6···O2, 3.001; O7···O1#5, 2.825; O7···O2#1, 2.705. #4: x, y, $1 + z$. #5: $1 - x$, $1 - y$, $-z$.

molecules fill the space between macrocycles. The macrocycles are linked by hydrogen bonds forming a 2-D layer, and all thiourea groups are involved in the hydrogen bond system, see Fig. 2A. The layers are directly stacked and connected by water molecules *via* hydrogen bond interactions, see Fig. 2B. X-Ray analysis reveals that complex **2** possesses a one dimensional single helical structure, which is consistent with the result derived from elemental analysis. The fundamental building unit of the crystal structure is shown in Fig. 3. It is composed of one zinc(II) center that is co-ordinated by two tu molecules (S1 and S2), two maleic anions (O1 and O4#; # = $\frac{1}{2} - x$, $-y$, $\frac{1}{2} + z$). Progression of the structure in the crystal employs this unit and its linkage motif using the remaining carboxylate oxygen atoms (O1#1, O4) on two maleic anion units. In this way, each maleic anion unit acts as a bidentate unit, linking two zinc atoms to yield a half turn unit of the helical structure. Extension of the structure in one dimension gives a 1-D helical Zn–maleate network as shown in Fig. 4. Here, zinc(II) ions in **2** are also in tetrahedral geometry; compared to **1**, the co-ordinated water molecule is replaced by a second thiourea. The Zn–O (1.961(5), 2.032(4), 2.033(4) Å for **1** and 1.951(3), 1.968(3) Å for **2**) and Zn–S (2.291(2) Å for **1** and 2.312(1), 2.370(2) Å for **2**) distances (Table 1) are similar to those observed for other zinc thiourea dicarboxylates.[10] Complex **2** possesses an interesting new motif for the helical supramolecular architecture, see Figs. 3 and 4. Remarkably, every turn of the helix bears four thiourea arms
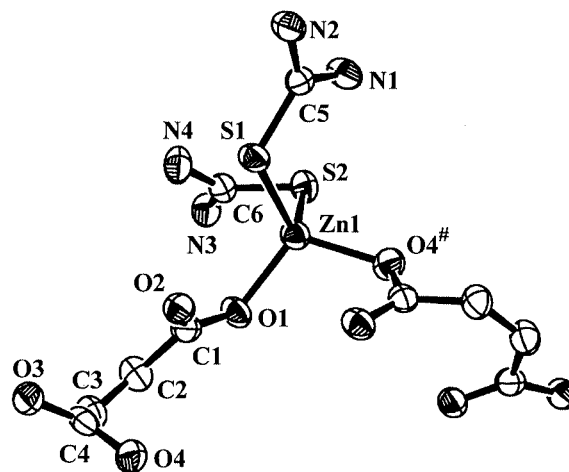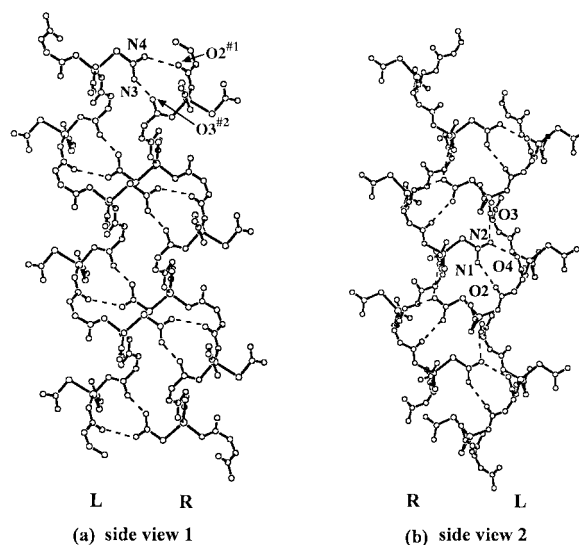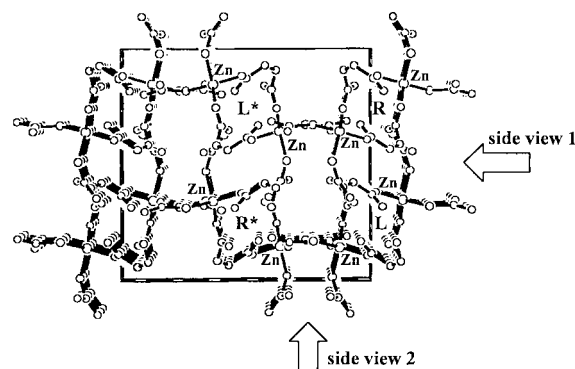
Fig. 3 Fundamental structure unit of complex **2** (#: $\frac{1}{2} - x$, $-y$, $\frac{1}{2} + z$).

L   R   R   L
**(a) side view 1**   **(b) side view 2**

(c) top view

Fig. 4 The infinite helical motif in complex **2**. **(a)**: Side view of the helical motif, relations and interhelix hydrogen bonds (dash line), mode 1, between helixes. Hydrogen bond lengths (Å) and angles (°): N4···O2#1, 2.997(4), 171.231; N3···O3#2, 2.869(4), 157.35. **(b)** Side view of the helical motif, relations and interhelix hydrogen bonds (dash line), mode 2, between helixes. Hydrogen bond lengths (Å) and angles (°): N2···O3#3, 2.918(5), 169.09; N2···O4#4, 2.848(4), 174.36; N1···O2#3, 2.843(4), 144.14. **(c)** Top view of the helix array. #1: $\frac{1}{2} + x$, y, $\frac{3}{2} - z$. #2: $1 - x$, $2 - y$, $1 - z$. #3: x, $\frac{3}{2} - y$, $z - \frac{1}{2}$. #4: $\frac{3}{2} - x$, $\frac{1}{2} + y$, z.

co-ordinated by zinc(II) ions, extending into four directions. Four arms of one helicate are inserted into the neighbouring four helixes. The outside part of each arm is an amino group (NH₂), with which hydrogen bonds involving carboxyl groups of the maleic anion are formed. It is these arms extending from the

**Table 1** Selected bond lengths (Å) and angles (°) of complexes **1** and **2**

1		**2**	
Zn(1)–O(3)	1.961(5)	Zn(1)–O(4)	1.968(3)
Zn(1)–O(1)	2.033(4)	Zn(1)–O(1)	1.951(3)
Zn(1)–O(5)	2.032(4)	Zn(1)–S(2)	2.370(2)
Zn(1)–S(1)	2.291(2)	Zn(1)–S(1)	2.312(2)
O(1)–Zn(1)–S(1)	112.7(1)	S(1)–Zn(1)–S(2)	113.35(4)
O(3)–Zn(1)–S(1)	123.2(1)	O(1)–Zn(1)–S(1)	113.77(8)
O(5)–Zn(1)–S(1)	111.4(1)	O(4)–Zn(1)–S(1)	114.22(9)
O(3)–Zn(1)–O(1)	103.3(2)	S(2)–Zn(1)–O(1)	101.79(9)
O(1)–Zn(1)–O(5)	94.0(2)	S(2)–Zn(1)–O(4)	99.85(9)
O(3)–Zn(1)–O(5)	108.1(2)	O(1)–Zn(1)–O(4)	112.4(1)
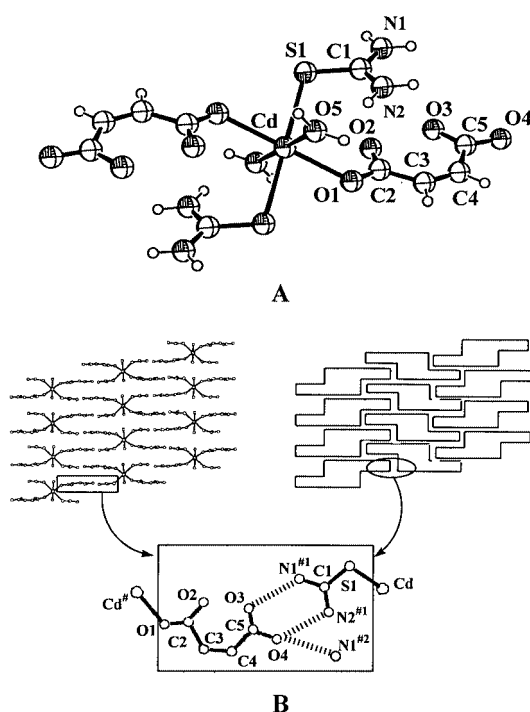
Fig. 5 **A**: Crystal structure of complex **3**. **B**: Rhombic 2-D sheet network in **3** and its hydrogen bond motif. Hydrogen bond data: N1#1···O3, 2.967 Å, 163.25°; N2#1···O4, 2.954 Å, 157.41°; N1#2···O4, 2.959 Å, 159.96°. #1: $x, \frac{1}{2} - y, z - \frac{1}{2}$. #2: $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$.

helix in four different directions and the associated hydrogen bond systems that induce and sustain four neighboring helixes, and also each helix is itself sustained by thiourea arms from four neighboring helixes. The mechanical coupling between neighboring helixes is very interesting and precise. Right-handed and left-handed helixes are assembled in pairs in **2**. Right-handed (R or R*) and left-handed (L or L*) helixes dot alternately in the helix array, and right-handed (or left-handed) helixes are surrounded by four left-handed (or right-handed) helixes, see Fig. 4. There are two kinds of interlacing modes between R–L helixes, Figs. 4(a) and (b). All helixes are linked *via* interhelix hydrogen bonds to form a 3-D hydrogen bonded framework. The pitch of the helix is 10.957(6) Å and the average diameter 4.50 Å smaller than that of cycle **1**, 5.30 Å.

Synthesis and structure of [Cd(Hmale)₂(tu)₂(H₂O)₂] 3 and [{(male)Cd(tu)₂}₂(male)Cd(tu)(H₂O)₂]ₙ 4

X-Ray analyses reveal that complex **3** possesses a hydrogen bonded distorted rhombic 2-D sheet structure (Fig. 5) and **4** a infinite single helical structure (Figs. 6 and 7). It is interesting that **3** and **4** are also time dependent and synthesized from the same solution source. The present results indicate that the rhombic 2-D sheet structure **3** is a kinetic product, formed
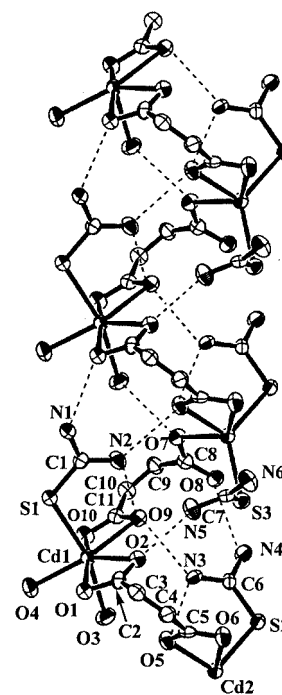
Fig. 6 Single helical structure of complex **4**. Hydrogen bond data: N1···O1#, 2.839(6), 151.65; N2···O5#, 2.976(7), 165.10; N2···O9, 2.955(7), 159.92; N3···O9, 2.921(7), 163.27; N4···O8, 2.860(6), 163.55; N5···O2, 2.964(7), 157.57; O3···O7#, 2.824(7) Å, 161.24. #: $1 + x, y, z$.
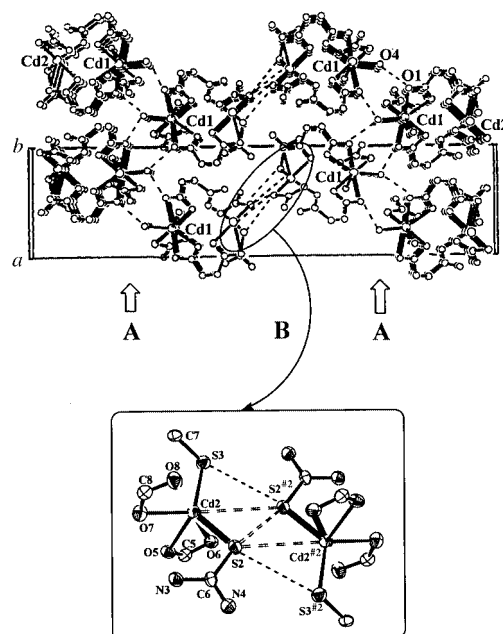
Fig. 7 Top view of the helical motif along the *a* axis and the weak interhelix interactions among helicates in complex **4**. **A**: Hydrogen bond interactions; O4···O1#1, 2.836(7) Å, 159.121°. **B**: Short S···S contacts; S2···S2#2, 3.145 Å; S2···S3#2, 3.800 Å; S2···Cd2#2, 3.627 Å. #1: $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. #2: $1 - x, 1 - y, 1 - z$.

reversibly from the components, which progressively converts into the thermodynamic product, the helicate **4**.[9]

In the structure **3**, cadmium(II) ion is connected by two maleic anions, two thioureas and two water molecules, Fig. 5A. The co-ordination unit acts as a structure unit assembling together *via* multiple hydrogen bonds between thiourea and carboxyl to form a highly ordered rhombic 2-D sheet network, Fig. 5B. All carboxyl groups and thiourea groups are packed nearly parallel in the sheet. Complex **4** possesses a single helical structure. The remarkable helical formation is sustained by a set of long route intrahelix hydrogen bonds between carboxyl and

Table 2 Selected bond lengths (Å) and angles (°) of complexes **3** and **4**

For **3**

Cd(1)–O(1)	2.374(4)	Cd(1)–O(1)	2.374(4)
Cd(1)–S(1)	2.617(2)	Cd(1)–S(1)	2.617(2)
Cd(1)–O(5)	2.405(7)	Cd(1)–O(5)	2.405(7)
S(1)–Cd(1)–S(1)	180.0	S(1)–Cd(1)–O(1)	78.9(1)
O(1)–Cd(1)–S(1)	101.1(1)	S(1)–Cd(1)–O(5)	86.3(1)
O(5)–Cd(1)–S(1)	93.7(1)	O(1)–Cd(1)–O(1)	180.0
O(1)–Cd(1)–O(5)	100.2(2)	O(5)–Cd(1)–O(1)	79.8(2)
O(5)–Cd(1)–O(5)	180.0		

For **4**

Cd(1)–S(1)	2.614(2)	Cd(1)–O(1)	2.462(4)
Cd(1)–O(2)	2.362(4)	Cd(1)–O(3)	2.388(4)
Cd(1)–O(4)	2.300(3)	Cd(1)–O(9)	2.505(4)
Cd(1)–O(10)	2.364(4)	Cd(2)–S(2)	2.516(2)
Cd(2)–S(3)	2.500(2)	Cd(2)–O(5)	2.334(4)
Cd(2)–O(6)	2.601(4)	Cd(2)–O(7)	2.321(3)
O(1)–Cd(1)–S(1)	93.33(9)	S(1)–Cd(1)–O(2)	99.73(10)
S(1)–Cd(1)–O(3)	163.8(1)	O(4)–Cd(1)–S(1)	88.4(1)
O(9)–Cd(1)–S(1)	95.02(10)	O(10)–Cd(1)–S(1)	92.48(10)
O(1)–Cd(1)–O(2)	54.5(1)	O(1)–Cd(1)–O(3)	89.3(2)
O(1)–Cd(1)–O(4)	85.4(1)	O(1)–Cd(1)–O(9)	134.1(1)
O(1)–Cd(1)–O(10)	169.2(1)	O(2)–Cd(1)–O(3)	94.8(1)
O(2)–Cd(1)–O(4)	139.2(1)	O(2)–Cd(1)–O(9)	79.6(1)
O(2)–Cd(1)–O(10)	133.1(1)	O(3)–Cd(1)–O(4)	75.9(2)
O(3)–Cd(1)–O(9)	94.6(1)	O(3)–Cd(1)–O(10)	82.7(1)
O(4)–Cd(1)–O(9)	139.8(1)	O(4)–Cd(1)–O(10)	85.7(1)
O(9)–Cd(1)–O(10)	54.2(1)	S(2)–Cd(2)–S(3)	130.56(5)
S(2)–Cd(2)–O(5)	110.55(10)	S(2)–Cd(2)–O(6)	90.43(10)
S(2)–Cd(2)–O(7)	100.44(9)	S(3)–Cd(2)–O(5)	112.1(1)
S(3)–Cd(2)–O(6)	95.5(1)	S(3)–Cd(2)–O(7)	111.09(9)
O(5)–Cd(2)–O(6)	52.9(1)	O(5)–Cd(2)–O(7)	79.4(1)
O(6)–Cd(2)–O(7)	131.6(1)	Cd(1)–S(1)–C(1)	109.8(2)

amino groups of thiourea. The helix has a straight line helical axis, a pitch of 8.13 Å and an average radius 2.51 Å [Typical α-helix in protein: pitch 5.4 Å, average radius 2.3 Å; hydrogen bond rings (R) $R^1_1(13)$; $R^a_d(n)$, a = number of acceptors, d = number of donors, n = number of relative atoms]. All carboxyl groups and thiourea molecules in the backbone are to involve hydrogen bond interactions. Six hydrogen bonded large rings spanning one or a half helical turn are observed as $R^1_1(18)$, $R^1_1(13)$, $R^1_1(11)$, $R^1_1(13)$, $R^1_1(18)$, $R^1_1(13)$ that strongly stabilize the helical structure.[11,12] The repeating unit in (**4**) contains four distinct single helixes, two pairs of right- and left-handed ones, forming an enantiomeric compound (Fig. 7). The right-handed helixes (left-handed helixes) are linked by interhelix hydrogen bonds to form a two dimensional sheet involving seven-co-ordinated Cd(1). Sheets of right- and left-handed helixes are linked by short S $\cdots$ S contacts (S2 $\cdots$ S2#2, 3.145; S2 $\cdots$ S3#2, 3.800 Å) and weak S2 $\cdots$ Cd(2)#2 (#2:1 − x, 1 − y, 1 − z) co-ordination (3.627 Å), Fig. 7. It is interesting that the helical structure contains two chemically distinct Cd atoms.[13] Atom Cd(1) is seven-co-ordinate by formation of bonds with four carboxyl oxygen atoms, two water and one thiourea molecule. Atom Cd(2) is 5 + 1 co-ordinate with three carboxyl oxygen atoms, two thiourea molecules and one weak interaction from the S atom of a neighboring helix. The atoms occupy two side positions of the helicate and make the repeating unit of the helix just one turn (14 atoms). Also, two maleate anions exhibit different co-ordination modes (tridentate and tetradentate), corresponding to two distinct Cd atoms, resulting in the different distances between Cd(1) $\cdots$ Cd(2) and Cd(1) $\cdots$ Cd(2)* (5.950(6) and 6.466(6) Å) (Fig. 6). Other bond distances and angles are given in Table 2.

Remarkably, the supramolecular structures of the zinc (**1**, **2**) and cadmium systems (**3**, **4**) are apparently different, especially as regards the infinite helical structures of **2** and **4**. In the structure **2**, all co-ordinated thiourea groups stretch out in different

directions and are involved in the *inter*helix hydrogen bond system by which the metallohelicate is stabilized. However, in **4**, co-ordinated thiourea groups are bent into the helicate itself and involved in the *intra*helix hydrogen bond system to stabilize the helicate formation. The main reason for this difference is the size of the metal ions and the rigidity of the maleic dianion. It shows us the versatility of the self-assembly process with multiple components.

In conclusion, a temperature and time dependent self-assembly process involving maleic dianion, thiourea and zinc or cadmium ion has been reported. By prolonging the reaction time and/or heating, the kinetic product **1** and **3** can be converted into the thermodynamic product **2** and **4**, respectively. Both thermodynamic products bear novel metallohelicate motifs which are induced and stabilized by interhelix hydrogen bonding for **2** and intrahelix hydrogen bonding for **4**. 3-D Networks are constructed in **2** and **4**. The helical structures in **2** and **4** are infinite and self-assembled by multiple components *via* hydrogen bond interactions. This probably provides a new approach for designing other new supramolecular assemblies and understanding the processes involved.

Experimental

Materials and methods

All starting materials were from commercial sources and used without further purification. Elemental analyses were carried out by Structure Research Laboratory, University of Science and Technology of China.

The crystal structures of complexes **1**–**4** were determined on a R-AXISII diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å). A laser-stimulated fluorescence image plate was used as a two-dimensional area detector. The data were corrected for Lorentz-polarization effects. The structures were solved by heavy-atom Patterson methods using the SAPI 91[14] for **1** and direct methods using the SIR 92[15] for **2**–**4** and refined by full-matrix least squares. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Scattering factors were taken from Cromer and Waber.[16] All calculations were performed using the TEXSAN crystallographic software package.[17] Crystal data are listed in Table 3.

CCDC reference number 186/1735.

See http://www.rsc.org/suppdata/dt/a9/a908070h/ for crystallographic files in .cif format.

Preparations

[{Zn(male)(tu)(H₂O)}₂]·4H₂O 1 and [{Zn(male)(tu)₂}ₙ] 2. Aqueous solutions (20 ml) of ZnSO₄·7H₂O (0.269 g, 1.0 mmol), maleic anhydride (0.114 g, 1.0 mmol) and thiourea (0.152 g, 2.0 mmol) were mixed and the pH value was controlled at 5–6. After stirring for 5 min the solution was divided into two portions. The first portion was slowly evaporated at room temperature, and the second heated to 100 °C for 5 min and then allowed to stand at room temperature. After 24 h, colorless plate crystals of complex **1** were produced from the first portion in high yield, and then, colorless needle-like crystals of **2** were precipitated from the same portion after several days. As the needle crystals of complex **2** appeared, the plate crystals of **1** slowly redissolved. In the second portion, colorless needle-like crystals of complex **2** were quantitatively isolated after several days. Calc. for **1**, C₅H₁₂N₂O₇SZn: C, 19.38; H, 3.88; N, 9.04. Found: C, 19.34; H, 3.90; N, 9.02%. Calc. for **2**, C₆H₁₀N₄O₄S₂Zn: C, 21.71; H, 3.02; N, 16.88. Found: C, 21.70; H, 3.05; N, 16.85%. Main IR bands: for complex **1**, 1193.0m ν(CN), ρ(NH₂); 1320.8s and 1407.7s ν(CN), ρ(NH₂), ν(CS); 1556.2s, 1635.6s $ν_{sym}(CO_2^-)$, $ν_{asym}(CO_2^-)$; 2850--3550s, ν(NH), ν(OH); for **2**, 1183.2w ν(CN), ρ(NH₂); 1295.5m, 1420.3m ν(CN), ρ(NH₂), ν(CS); 1514.8m, 1581.7s, 1641.6s $ν_{sym}(CO_2^-)$,

Table 3 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_5H_{12}N_2O_7SZn$	$C_6H_{10}N_4O_4S_2Zn$	$C_{10}H_{18}CdN_4O_{10}S_2$	$C_{11}H_{20}Cd_2N_6O_{10}S_3$
Formula weight	309.60	331.67	528.79	717.31
Crystal symmetry	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$Pbca$	$P2_1/c$	$P2_1/n$
$T/°C$	−100	−100	−100	−100
$a/Å$	9.087(9)	14.48(1)	5.804(2)	8.238(6)
$b/Å$	9.859(10)	15.64(1)	24.97(2)	8.134(6)
$c/Å$	6.87(1)	10.957(6)	6.190(5)	34.57(5)
$a/°$	108.65(8)			
$\beta/°$	96.21(5)		92.90(6)	92.51(5)
$\gamma/°$	97.77(9)			
Z	2	8	2	4
$V/Å^3$	570(1)	2481(1)	895(1)	2314(1)^3
μ/cm^{-1}	23.57	23.24	15.13	21.70
$R[F_o^2 > 2\sigma(F_o^2)]$	0.072	0.052	0.0653	0.0512
$R'[F_o^2 > 2\sigma(F_o^2)]$	0.119	0.079	0.0995	0.0832

$v_{asym}(CO_2^-)$; 3135.4m, 3195.5s, 3314.7s, 3401.5m $v(NH)$ (hydrogen bonded and free groups).

[Cd(Hmale)(tu)$_2$(H$_2$O)$_2$] 3 and [{(male)Cd(tu)$_2$}$_2$(male)-Cd(tu)(H$_2$O)$_2$]$_n$ 4. Aqueous solutions (20 ml) of CdSO$_4$ (0.316 g, 1.0 mmol), maleic anhydride (0.114 g, 1.0 mmol) and thiourea (0.152 g, 2.0 mmol) were mixed and the pH value was controlled at 6. The solution was slowly evaporated at room temperature (about 10 °C). After two days, colorless plate crystals of complex **3** were produced. Several days later colorless needle-like crystals of complex **4** were quantitatively isolated when **3** gradually disappeared. Calc. for **3**, $C_{10}H_{18}CdN_4O_{10}S_2$: C, 22.61; H, 3.39; N, 10.55. Found: C, 22.54; H, 3.41; N, 10.72%. Calc. for **4**, $C_{11}H_{20}Cd_2N_6O_{10}S_3$: C, 18.06; H, 3.51; N, 14.04. Found: C, 18.12; H, 3.56; N, 14.12%. Main IR bands: for complex **3**, 1193.0m $v(CN)$, $\rho(NH_2)$; 1320.8s and 1407.7s $v(CN)$, $\rho(NH_2)$, $v(CS)$; 1556.2s, 1635.6s $v_{sym}(CO_2^-)$, $v_{asym}(CO_2^-)$; 2850–3550s, $v(NH)$, $v(OH)$. For **4**, 1183.2w $v(CN)$, $\rho(NH_2)$; 1295.5m, 1420.3m $v(CN)$, $\rho(NH_2)$, $v(CS)$; 1514.8m, 1581.7s, 1641.6s $v_{sym}(CO_2^-)$, $v_{asym}(CO_2^-)$; 3135.4m, 3195.5s, 3314.7s, 3401.5m $v(NH)$ (hydrogen bonded and free groups).

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