Solvent dependent assembly and disassembly of a hydrogen bonded helical structure in a Co–Mo bimetallic complex†

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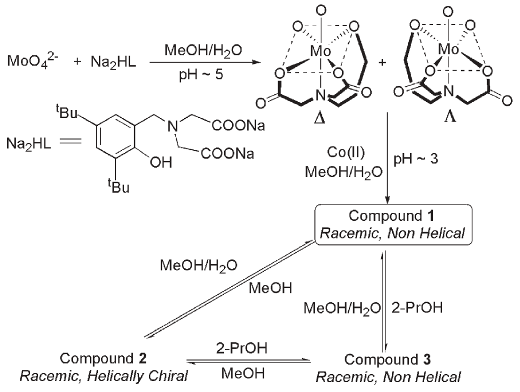
The effect of solvent on the assembly and disassembly of a hydrogen bonded helical structure in a bimetallic cobalt complex of a molybdenum-containing metalloligand and their spontaneous resolution has been demonstrated.

Helicity is of prime importance in natural and synthetic materials.[1] This has prompted the synthesis of artificial helical structures.[2] The importance of hydrogen bonding interactions in supramolecular chemistry and biology has been emphasized in the literature.[1] Although there are reports on supramolecular assembly of coordination complexes through hydrogen bonding,[3a] reports on hydrogen bonded (H-bonded) helical structures in coordination compounds are limited.[3b,3c] The construction of helical structures and their spontaneous resolution without using any chiral auxiliary remains a challenge.[4] The role of the solvent in the H-bonded network structure has not been widely studied.[4d] Herein we report the spontaneous resolution of a racemic but helically chiral compound $[(MoO_2L)Co(H_2O)_4(MeOH)]^+[MoO_2L]^-\cdot2H_2O\cdot MeOH$ (**2**) {L = carboxymethyl(3,5-di-*tert*-butyl-2-hydroxybenzyl)-aminoacetate} and the effect of external stimuli such as solvent on its assembly/disassembly leading to racemic non-helical compounds, $[Co(H_2O)_6]^{2+}2[MoO_2L]^-\cdot3H_2O$ (**1**) and $[(MoO_2L)_2Co(H_2O)_4][\{Co(H_2O)_6\}\{MoO_2L\}_2]\cdot4H_2O\cdot2^iPrOH$ (**3**). Akin to our previous report,[5] the strategy is to synthesize the metalloligand, $[MoO_2L]^-$, from the tetradentate tribasic ligand L and use this for binding other transition metal ions.

Reaction of ligand L with MoO_4^{2-} generated racemic $[MoO_2L]^-$ *in situ*, which, on reaction with $CoCl_2\cdot6H_2O$ (pH was found to be ∼3 at this stage), formed compound $[Co(H_2O)_6]^{2+}2[MoO_2L]^-\cdot3H_2O$ (**1**) in high yield (Scheme 1). Compound **2** and **3** were obtained by the recrystallization of vacuum dried **1** from MeOH and 2-propanol, respectively (see ESI†).



Scheme 1

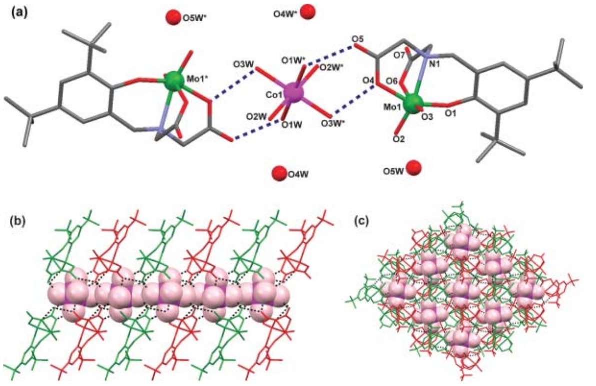
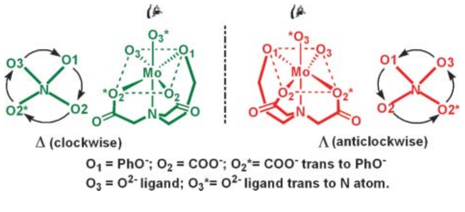


Fig. 1 (a) Molecular structure of the compound **1**. View of the heterochiral 2D H-bonded packing (b) along the *b*-axis and (c) along the *c*-axis. Colour: two enantiomers of the metalloligand: green (clockwise) and red (anticlockwise); Co bonded H_2O: light pink. Dotted line: H-bond.

X-Ray analysis‡ reveals that, compound **1** crystallizes in the monoclinic space group $P2_1/a$. In **1**, the Mo center of the metalloligand is octahedrally coordinated to two *cis*-oxo ligands and the tripodal tetradentate OONO donor ligand, L. The Co(II) centre in **1** is coordinated to six aqua ligands (Fig. 1a). The metalloligands remain free and are not coordinated to the Co(II) center. Due to the asymmetric coordination of the organic ligand to the molybdenum center in the $[MoO_2L]^-$, there exists molecular chirality (Δ and Λ)[6] (Scheme 2). The Co(II) coordinated water molecules and solvent water molecules show H-bonding interactions with carboxylate oxygens of the metalloligands and form a



Scheme 2

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† Electronic supplementary information (ESI) available: Synthesis, tables of X-ray data, bond distances and angles, ORTEP, additional figures and CD spectra. See DOI: 10.1039/b705891h

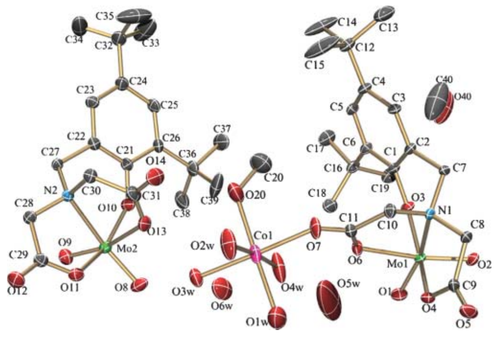

Fig. 2 ORTEP view of **2a** with 30% thermal ellipsoid probability.

2D H-bonded network (Fig. 1b & 1c). Both the enantiomers of the metalloligand are present in the unit cell and the compound can be described as a racemate.

As the compound **1** was obtained in an acidic medium, it is not surprising that the Co(II) center is coordinated to six aqua ligands. Thus, it was expected that recrystallization of **1** from various alcohols would provide compounds exhibiting different H-bonded networks. As observed in our earlier work,[5] recrystallization of **1** from methanol resulted in a helical H-bonded structure, **2**, which crystallizes in the monoclinic non-centrosymmetric space group $P2_1$. The Co(II) center is coordinated to four aqua ligands, one methanol oxygen (*cis* to O7), and a carboxylate oxygen, O7, of the metalloligand (Fig. 2). Another carboxylate oxygen, O6, of the metalloligand is H-bonded to one of the Co(II) bound waters, O4W. The other two carboxylate oxygens, O4 and O5, are H-bonded with Co(II) bound waters, O2W and O3W, of the neighbouring unit. Due to the *cis*-disposition of the carboxyl groups involved in H-bonding, an infinite helical chain around a crystallographic 2_1 screw axis is formed (Fig. 3a) (see ESI†). One metalloligand remains free and this also forms a helical chain around a 2_1 screw axis (Fig. 3b). The two helices are held together by H-bonding interactions involving lattice waters (O5W and O6W) and methanol oxygen (O40) and thus the helical chirality is transmitted into the whole 2D sheet (Fig. 3c). These H-bonding interactions are responsible for homochiral crystal packing and spontaneous resolution of **2**. Although both the enantiomers of the metalloligand are present in the unit cell, the compound is chiral due to the helix formation. Both the enantiomers, *P* (**2a**), and *M* (**2b**) helices, were isolated and structurally characterized. The Flack parameters [−0.01(3) (**2a**) and 0.01(4) (**2b**)] clearly show that each crystal is enantiomerically pure. This is a rare example where the racemic compound containing two metalloligand enantiomers is spontaneously resolved due to the H-bonded helix formation.

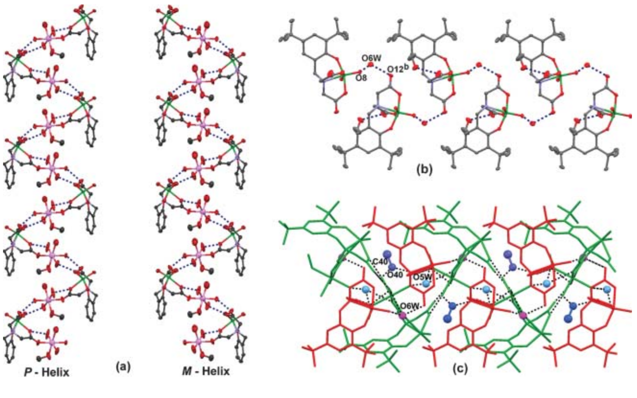

Fig. 3 View of (a) 1D heterobimetallic H-bonded helix in **2a** (*P*) and **2b** (*M*) along *a*-axis. H atoms and the *tert*-butyl groups are omitted for clarity. (b) View of 1D right handed helix (*P*-helix) of free metalloligand in **2a** along the *a*-axis. (c) 2D H-bonded network **2a** along the *a*-axis.

Control of the chirality in this type of compound is a challenging task. In the present case, crystals of **2b** were obtained selectively, by the addition of a small amount of D-glucose during crystallization. It is suggested that, in solution, D-glucose preferentially adsorbs the Δ isomer of the metalloligand and prevents its binding towards the Co(II) center. Thus, binding of the Λ metalloligand towards the Co(II) center is favoured at the time of nucleation. Due to the strong H-bonding interactions, the *M*-helical isomer appears first.[7] Although controlled crystallization has been reported in organic compounds by the addition of small amount chiral impurity,[8] there is no such report on preferential crystallization of H-bonded helical isomers in coordination chemistry.[9]

Recrystallization of **1** from 2-propanol is expected to afford a different H-bonded network structure. Thus, recrystallization of **1** from 2-propanol afforded the compound **3**. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. It is composed of two types of molecular entity, $[(MoO_2L)_2Co(H_2O)_4]$ and $[Co(H_2O)_6]^{2+}2[MoO_2L]^-$. Two enantiomers of $[MoO_2L]^-$ units are present in each of the molecular entities (Fig. 4a). In the $[(MoO_2L)_2Co(H_2O)_4]$ unit, the Co(II) is coordinated to two symmetrically equivalent carboxylate oxygens (O7 and O7*) of the two metalloligands, and four water oxygens (O1W, O1W*, O2W and O2W*). In the $[(MoO_2L)_2Co(H_2O)_4]$ unit, the inter-unit

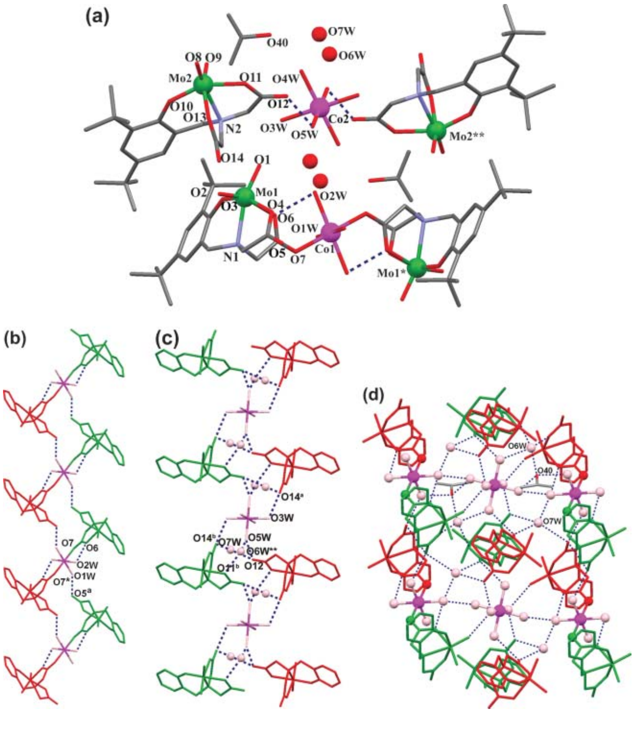

Fig. 4 (a) Crystal structure of **3**. View of (b) 1D H-bonded zigzag chain of $[(MoO_2L)_2Co(H_2O)_4]$ along the *b*-axis. (c) 1D H-bonded chain formed by $[Co(H_2O)_6]^{2+}$, metalloligand enantiomers and solvent along the *b*-axis. (d) 2D H-bonded racemic packing along the *c*-axis. Symmetry: *: $-x, -y, 1 - z$; **: $-x, 1 - y, 1 - z$; *a*: $-1 + x, y, z$; *b*: $1 - x, 1 - y, 1 - z$.

H-bonding interactions are present and an 1D isotactic zigzag H-bonded chain is formed along the *a*-axis (Fig. 4b). The structural features of the $[Co(H_2O)_6]^{2+}2[MoO_2L]^-$ unit are similar to those of **1**. This also forms a 1D H-bonded chain (Fig. 4c) along the *a*-axis. Two solvent waters, O(6W) and O(7W) and solvent 2-propanol, are engaged in H-bonding interactions, which connect two heterochiral chains (Fig. 4d) and a 2D H-bonded network is formed. Due to such heterochiral close packing this compound crystallizes in a racemic form.

To examine the retention of the helical chirality in **2** we have studied the solvent dependent interconversion among the three compounds. Compound **1**, on recrystallization from methanol, undergoes reaction with one free metalloligand and produces **2**, a H-bonded helical chain, wherein a methanol becomes coordinated to the Co(II) center. When **1** is recrystallized from 2-propanol, compound **3** is obtained, where both the metalloligands are coordinated to the Co(II) center but 2-propanol is not coordinated like methanol in **2**. This difference may be attributed to the different stereoelectronic behaviour of the solvent used for crystallization. The methanolic solution of **3**, on slow evaporation, affords the helically chiral **2** and *vice versa*. Interestingly, compounds **2** or **3** can be reconverted to **1** by dissolution in aqueous methanol (pH ∼ 3)§. All the compounds form 2D H-bonded networks in the crystal, however, the H-bonded structure depends upon the solvent of crystallization and methanol is the only solvent from which helically chiral compound is obtained. The reason behind the interconversion is the labile nature of the Co(II) center for the ligand substitution reaction through a bond rapture mechanism.

Solid state diffuse reflectance CD (DRCD) and transmission CD spectra of crystals of **2a** and **2b** were measured to detect the supramolecular chirality. In the DRCD measurement, apparent CD signals appeared due to macroscopic anisotropies (linear birefringence and linear dichroism). Thus, the obtained CD signal is not true CD. Although the absorption peak was observed, the Cotton effect was very weak (see ESI†). Optical activity is generally originated from the molecular and supramolecular chirality. However, due to the presence of both of the isomers (Δ and Λ), the chirality originated from the molecule is cancelled out (Scheme 2). Compound **2** has only the helical chirality.

In summary, three heterobimetallic compounds, two racemic non-helical and one racemic but helically chiral, have been synthesized from a racemic metalloligand. Compound **2** is a rare example where a racemate spontaneously resolves due to H-bonded helical chain formation. Further, we are able to control the chirality and selectively crystallize the desired helical isomer. The effect of the solvent on the assembly and disassembly process of the H-bonded helical structure in a coordination compound is demonstrated. Separation of the enantiomers, Δ and Λ, the synthesis of chiral helical polymers from them and interconversion between the two helicate forms (*P* and *M*) are presently underway and will be reported in due course.

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Notes and references

‡ Crystal data for **1**: $C_{38}H_{70}CoMo_2N_2O_{23}$, $M_W = 1173.77$, $T = 293(2)$ K, monoclinic, $P2_1/a$, $a = 12.156(9)$ Å, $b = 9.139(7)$ Å, $c = 23.765(12)$ Å, $\beta = 95.00(9)°$, $V = 2630(3)$ Å^3. $Z = 2$, $\rho_{calcd} = 1.482$, $\mu = 0.858$, $\lambda = 0.71073$ Å, $2\theta_{max} = 49.96$, reflection collected/unique = 5192/4767, $R_{int} = 0.0000$, $R1 = 0.1036$, $wR2 = 0.2681$ for 2759 reflections $[I > 2\sigma(I)]$. Three C atoms (C13, C14 and C15) are disordered. **2a**: $C_{40}H_{72}Mo_2N_2CoO_{22}$, $M_W = 1183.81$, $T = 293(2)$ K, monoclinic, $P2_1$, $a = 13.735(3)$ Å, $b = 11.739(11)$ Å, $c = 16.805(11)$ Å, $\beta = 96.529(9)°$, $V = 2691.9(6)$ Å^3. $Z = 2$, $\rho_{calcd} = 1.461$, $\mu = 0.837$, $\lambda = 0.71073$ Å, $2\theta_{max} = 49.94$, reflection collected/unique = 5203/4980, $R_{int} = 0.0097$, $R1 = 0.0421$, $wR2 = 0.1082$ for 4488 reflections $[I > 2\sigma(I)]$, Flack(x) parameter = −0.01(3). **2b**. $C_{40}H_{72}Mo_2N_2CoO_{22}$, $M_W = 1183.81$, $T = 293(2)$ K, monoclinic, $P2_1$, $a = 13.792(2)$ Å, $b = 11.692(2)$ Å, $c = 16.692(5)$ Å, $\beta = 96.428(8)°$, $V = 2674.8(10)$ Å^3. $Z = 2$, $\rho_{calcd} = 1.452$, $\mu = 0.842$, $\lambda = 0.71073$ Å, $2\theta_{max} = 49.96$, reflection collected/unique = 5161/4944, $R_{int} = 0.0265$, $R1 = 0.0525$, $wR2 = 0.1084$ for 3284 reflections $[I > 2\sigma(I)]$, Flack(x) parameter = 0.01(4). **3**: $C_{82}H_{148}Co_2Mo_4N_4O_{44}$, $M_W = 2395.68$, $T = 293(2)$ K, triclinic, $P\bar{1}$, $a = 10.126(15)$ Å, $b = 13.08(17)$ Å, $c = 22.454(10)$ Å, $\alpha = 73.8(3)°$, $\beta = 77.93(3)°$, $\gamma = 81.74(11)°$, $V = 2781.5(13)$ Å^3. $Z = 1$, $\rho_{calcd} = 1.430$, $\mu = 0.811$, $\lambda = 0.71073$ Å, $2\theta_{max} = 49.96$, reflection collected/unique = 10383/9771, $R_{int} = 0.0262$, $R1 = 0.0560$, $wR2 = 0.1624$ for 6925 reflections $[I > 2\sigma(I)]$. CCDC 640669–640672. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705891h

§ Formation of these compounds is confirmed by single crystal unit cell determination and powder X-ray diffraction studies (for **1** and **2**, see ESI†)

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