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Metal-ion-directed synthesis of sulfur-based macrocyclic helicates

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Schiff-base condensation of pyridine-2,6-dicarbaldehyde and 2-[(2-{[(2-aminophenyl)sulfanyl]methyl}benzyl)sulfanyl]aniline led to different helical macrocyclic products depending on the template metal ion; a *mono*-helical [1 + 1] macrocyclic complex was generated in the presence of Ag^I and a *double*-helical [2 + 2] macrocyclic complex was generated in the presence of Cd^{II}.

Substantial interest surrounds the application of metal ions in the control of entwined molecular architectures and in particular in the production of helical metal complexes, the helicates.[1] While a large number of single-, double- and even triple-helicate species are now known, relatively few macrocyclic helicate systems, which are potentially more robust in solution, have been reported.[2,3] We have used convergent pyridyl-2,6-diimine units as nuclei for macrocyclic helicates to prepare a range of novel double helical complexes with potentially ‘tunable’ secondary structures.[3] We are now incorporating S donors into related macrocyclic species, envisaging that, in addition to changing the binding characteristics of the ligands, these donors may affect the folding characteristics of the macrocycle, thereby influencing the secondary structures of any helical products. Schiff-base condensations of pyridine-2,6-dicarbaldehyde with the new α,ω-diamine **I** show an unexpected dependence on the metal ion and generate different helical products (Scheme 1).

Reactions of **I** with pyridine-2,6-dicarbaldehyde in the presence of hydrated silver or cadmium perchlorates were carried out in MeOH solution under similar conditions. The yellow microcrystalline products precipitated in good yield, each reaction mixture afforded, after recrystallisation, mononuclear complexes of, respectively, [1 + 1] and [2 + 2] condensation products.‡ Remarkably, the larger macrocyclic product is produced with the *smaller* metal ion template, indicating that the different metal-ion affinities for the soft sulfur donors controls the course of the cyclocondensation and generates a *mono*-helical [1 + 1] product **1** with silver(I) and a *double*-helical [2 + 2] product **2** with cadmium(II). X-Ray structural data obtained for each complex shows that different metal–sulfur interactions are a key feature of the resulting complexes.

X-Ray structural analysis of **1**§ confirms the presence of the quinquedentate [1 + 1] cyclocondensation ligand in the $[Ag(L^1)]^+$ cation and shows that all the potential donors of the ligand co-ordinate to the metal ion (Fig. 1). Strong metal–sulfur bonding interactions in the complex reflect a donor–acceptor complementarity consistent with hard–soft acid–base criteria. The co-ordination geometry in the complex is intermediate between trigonal bipyramidal and square pyramidal and involves a displacement of S donors 1.58 and 0.89 Å above and below the N_3 plane of the essentially planar pyridyl-2,6-diimine unit. Such an arrangement produces a *single* helical species similar to related semi-rigid N_3S_2 complexes.[5]

In contrast, the X-ray structure of **2**¶ confirms that the template reaction of **I** with pyridine-2,6-dicarbaldehyde generates the new [2 + 2] N_6S_4 ligand in the presence of Cd^{II} (Fig. 2). The distorted octahedral N_6 metal environment in the *double* helical $[Cd(L^2)]^{2+}$ cation results from *trans*-meridional co-ordination of the two pyridyl-2,6-diimine units of the ligand. Our previous studies with related systems have identified that such an arrangement generates a double helical binding domain, which acts as a nucleus for the molecular helicity in macrocyclic complexes.[3] The twisting of the ligand in the complexes resembles that of its N_6O_4 double helicate analogues and, remarkably, the arrangement of the exocyclic aromatic rings is similar in both types of complex. In this case, however the S atoms modify the double helix so that the rings lie in less favoured positions for

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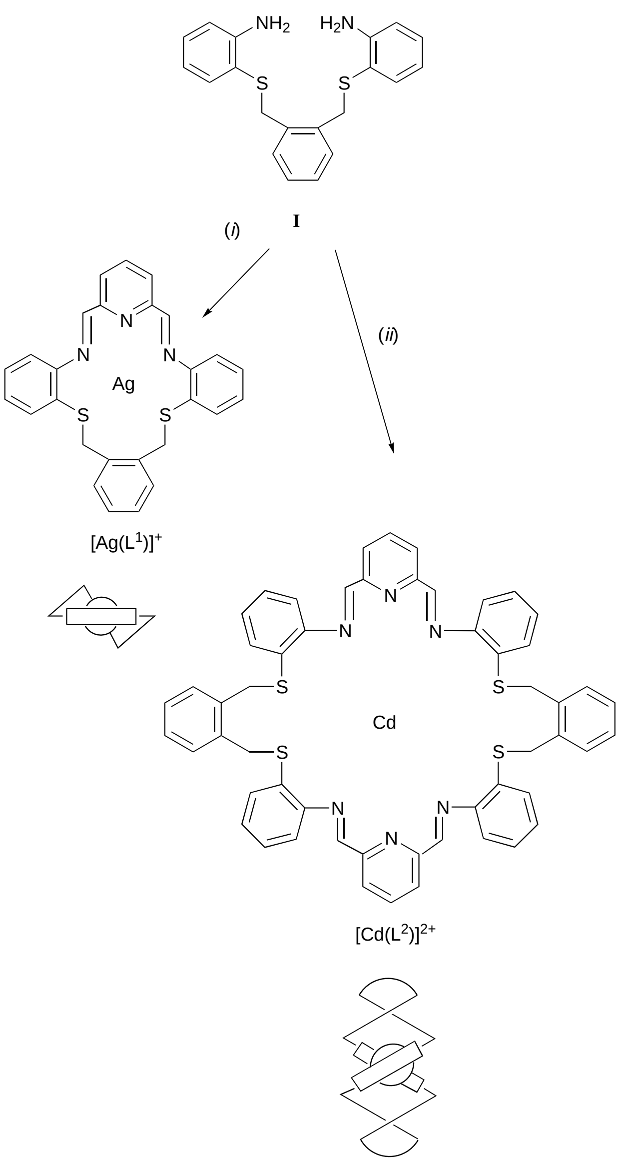
‡ 2-[(2-{[(2-Aminophenyl)sulfanyl]methyl}benzyl)sulfanyl]aniline (0.67 g, 5 mmol in 50 cm^3 MeOH) was added dropwise to a refluxing methanol solution of pyridine-2,6-dicarbaldehyde (0.68 g, 5 mmol) and the appropriate hydrated metal perchlorate [$Ag(ClO_4)\cdot H_2O$ (10 mmol) or $Cd(ClO_4)\cdot 6H_2O$ (5 mmol)]. The yellow microcrystalline solids resulting in each case were isolated and recrystallised from MeCN (**1**) or from dimethylformamide (dmf)–H_2O (**2**). **CAUTION:** metal perchlorate salts are potentially explosive and should be handled with care.

$[Ag(L^1)][ClO_4]$ **1**: (2.78 g, 84%) (Found: C, 49.5; H, 3.3; N, 6.5. Calc. for $C_{27}H_{21}AgClN_3O_4S_2$: C, 49.2; H, 3.2; N, 6.4%). Mass spectrum [fast atom bombardment (FAB), positive ion]: *m/z* 560 {100%, $[Ag(L^1)]^+$}. NMR (250 MHz, CD_3CN, ambient): δ_H 8.92 [2 H, d, $^3J(^{107,109}AgH)$ 3.7 Hz, imine CH], 8.31 (1 H, dd, γ-py*H*), 8.06 (2 H, d, β-py*H*), *ca.* 8.14–8.07 (2 H, m, SC_6H_4N), *ca.* 7.64–7.55 (6 H, m, SC_6H_4N), 7.40 and 7.15 [4 H, m, $C_6H_4(CH_2)_2$], 4.67 (4 H, s, CH_2).

$[Cd(L^2)][ClO_4]_2\cdot$dmf **2**: (2.18 g, 68%) (Found: C, 51.9; H, 3.7; N, 7.9. Calc. for $C_{57}H_{49}CdCl_2N_7O_9S_4$: C, 53.2; H, 3.8; N, 7.6%). Mass spectrum (FAB, positive ion): *m/z* 1116 {20%, $[Cd(L^2)(ClO_4)]^+$}, 1017 {100, $[Cd(L^2)]^+$}. NMR (300 MHz, CD_3CN, 298 K): δ_H 8.43 [2 H, t, ^3J(HH) 7.8, satellites $^5J(^{111,113}CdH)$ 2.7, γ-py*H*], 8.22 [4 H, br s, satellites $^3J(^{111,113}CdH)$ *ca.* 11, imine CH], *ca.* 7.98 [4 H, d, ^3J(HH) 7.8, β-py*H*], 7.97 [s, $HCON(CH_3)_2$], *ca.* 7.51–7.33 and 6.79 (16 H, SC_6H_4N), 6.88 and 6.22 [8 H, m, $C_6H_4(CH_2)_2$], 4.02 and 3.42 [8 H, AB, ^2J(HH) 12.5 Hz, CH_2], 2.93 and 2.81 [$HCON(CH_3)_2$].

§ Crystal data for $[Ag(L^1)][ClO_4]$ **1**: $C_{27}H_{21}AgClN_3O_4S_2$, $M = 658.91$, monoclinic, space group $P2_1/n$, $a = 12.4236(7)$, $b = 7.4619(6)$, $c = 27.5473(13)$ Å, $\beta = 94.191(5)°$, $U = 2546.9(3)$ Å^3, $Z = 4$, $F(000) = 1328$, $D_c = 1.718$ g cm^{-3}, μ(Cu-Kα) = 9.196 mm^{-1}, λ(Cu-Kα) = 1.541 78 Å. A total of 4667 reflection data were collected with a Siemens P4 four-circle diffractometer using a θ–2θ scan mode in the θ range 3.22–56.75° from a yellow crystal (0.16 × 0.16 × 0.10 mm) mounted on a quartz fibre. The structure was solved by direct methods and refined on F^2 for 3394 independent absorbance-corrected reflections ($R_{int} = 0.0631$, T_{max} 0.349, T_{min} 0.248).[4] With the exception of disordered oxygens of the perchlorate anion, all non-H atoms were modelled with anisotropic displacement parameters and refinement converged at *R*1 0.0675, *wR*2 0.0979 [$I > 2\sigma(I)$] and *R*1 0.1534, *wR*2 0.1288 (all data).

¶ Crystal data for $[Cd(L^2)][ClO_4]_2\cdot 1.5dmf\cdot H_2O$ **2**: $C_{58.5}H_{53.5}CdCl_2N_{7.5}O_{10.5}S_4$, $M = 1341.13$, monoclinic, space group $P2_1/n$, $a = 10.910(3)$, $b = 23.819(5)$, $c = 23.147(5)$ Å, $\beta = 91.01(2)°$, $U = 6014(3)$ Å^3, $Z = 4$, $F(000) = 2748$, $D_c = 1.481$ g cm^{-3}, μ(Mo-Kα) = 0.656 mm^{-1}, λ(Mo-Kα) = 0.710 73 Å. A total of 13 036 reflection data were collected as above in the θ range 1.23–25.00° from a yellow crystal (0.44 × 0.44 × 0.42 mm) mounted in a Lindemann tube under mother-liquor. The structure was solved by the Patterson superposition method and refined on F^2 for 10 579 independent absorbance-corrected reflections ($R_{int} = 0.0769$, T_{max} 0.612, T_{min} 0.566).[4] Anisotropic displacement parameters were assigned to all non-H atoms of full occupancy. Refinement converged at *R*1 0.0759, *wR*2 0.1616 [$I > 2\sigma(I)$] and *R*1 0.1978, *wR*2 0.2492 (all data). CCDC reference number 186/655.



Scheme 1 Synthesis of macrocyclic single and double helicates: (*i*) pyridine-2,6-dicarbaldehyde, $Ag(ClO_4)\cdot H_2O$, MeOH; (*ii*) pyridine-2,6-dicarbaldehyde, $Cd(ClO_4)_2\cdot 6H_2O$, MeOH

strong π–π interactions and the $C_6H_4(CH_2)_2$-*o* units are somewhat extruded from the central (metal-binding) domain of the complex. Long Cd · · · S distances in the complex (2.99–3.93 Å) indicate little metal–sulfur interaction and the pitch of the resulting double helix is significantly extended in comparison with the N_6O_4 analogue (*ca.* 9.8 *vs. ca.* 8.8 Å).

As might be expected, the different helicates show very different behaviour in solution. At ambient temperature the ^1H NMR spectrum of compound **1** in CD_3CN shows that the complex has effectively two-fold symmetry in solution. The imine proton signal appears as a doublet due to $^{107/109}Ag$–^1H coupling, confirming that the complex is inert to metal exchange on the NMR time-scale. The singlet observed for the methylene protons is attributed to interconversion of enantiomers of the chiral single helicate.

In contrast, the ambient-temperature ^1H NMR spectrum of compound **2** in CD_3CN (Fig. 3) shows an AB subspectrum for the methylene protons consistent with retention of molecular helicity in solution. In this case, the spectrum indicates effective four-fold symmetry for the complex. On lowering the temperature, the four-fold symmetry of the complex breaks down and the proton signals of $[Cd(L^2)]^{2+}$ broaden (while solvate signals remain sharp). Several resonances are observed to split symmetrically (Δδ *ca.* 0.6–1.7 ppm) about the positions of the signals at ambient temperature (Fig. 3). The widely differing proton environments indicated by these shifts correlate closely with those of the effectively two-fold symmetric solid-state structure; *e.g.* imine and $C_6H_4(CH_2)_2$-*o* protons each have two significantly different environments in the crystal, one lies in the shielding cone of an adjacent aromatic ring and the other is

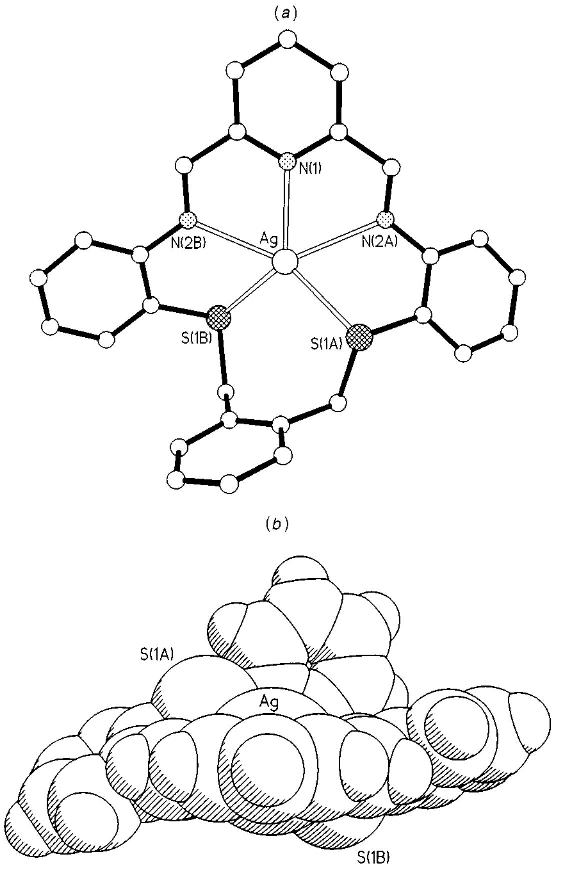


Fig. 1 Structure of the single helicate $[Ag(L^1)]^+$ in **1**: (*a*) a view onto the N_3 plane showing the deployment of all donors of the quinquedentate ligand, Ag–N(1) 2.365(8), Ag–N(2A) 2.524(9), Ag–N(2B) 2.458(9), Ag–S(1A) 2.590(3), Ag–S(1B) 2.612(3) Å; (*b*) a view down the N(1)–Ag vector showing the single helical configuration of the complex

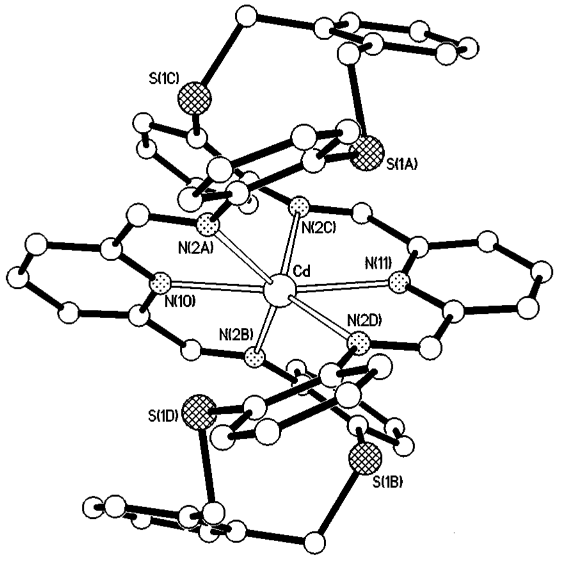


Fig. 2 Structure of the double helicate $[Cd(L^2)]^{2+}$ in **2**: Cd–N(10) 2.266(7), Cd–N(11) 2.257(7), Cd–N(2A) 2.443(8), Cd–N(2B) 2.548(7), Cd–N(2C) 2.602(8), Cd–N(2D) 2.417(8), Cd · · · S(1A) 3.21, Cd · · · S(1B) 3.58, Cd · · · S(1C) 3.93, Cd · · · S(1D) 2.99 Å; N(10)–Cd–N(11) 150.7(3)°. The dihedral angle between N_3 planes of pyridyl-2,6-diimine units 56.0°

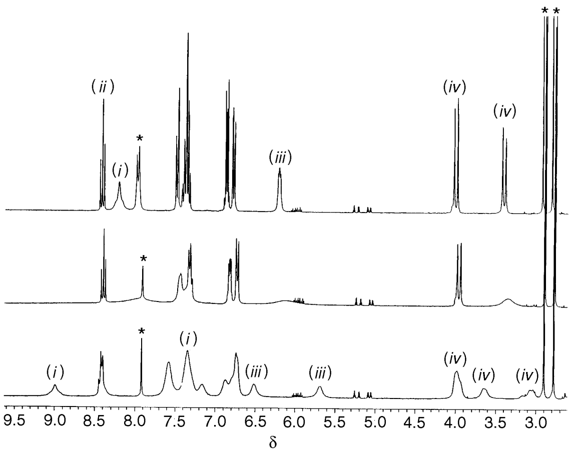


Fig. 3 The ^{1}H NMR spectrum of $[Cd(L^2)]^{2+}$ in CD_3CN at selected temperatures: (*i*) imine CH, (*ii*) γ-py*H*, (*iii*) $C_6H_4(CH_2)_2$, (*iv*) CH_2; signals from dmf solvate are indicated with an asterisk

positioned well away from such shielding effects. Overall, the low-temperature spectrum is consistent with a species of C_2 symmetry similar to the fully twisted macrocycle array observed in the solid state, giving the first evidence for the existence of a fully-twisted macrocyclic helicate in solution. Observations of $^{111/113}$Cd coupling to the γ-pyridyl protons confirm that the complex is inert to metal exchange throughout the temperature range investigated. We envisage that the exchange process that averages these signals at ambient temperature but retains the helicity of the complex and the co-ordination of the metal involves an interchange of aromatic ring positions through a concerted 'slipping' of the macrocyclic ring. We are currently investigating the role different donor sets play in stabilising related helicate structures in solution.

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