PAPER

Synthesis of ligands containing N-oxide donor atoms and their assembly into metallosupramolecular structures†

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A series of ligands that contain both N-donor and N-oxide donor atoms have been synthesised and ligands L^5, L^6, L^7 and L^8 contain, 4, 6, 5, and 6 donor atoms respectively. The smallest ligand L^5 forms a mononuclear complex with Cu^{2+} ([Cu(L^5)(ClO$_4$)$_2$(MeCN)]) whereas L^6 and L^7 form dinuclear double helicates with Ni^{2+} and Cu^{2+} respectively ([Ni$_2$(L^6)$_2$]$^{4+}$ and [Cu$_2$(L^7)$_2$]$^{4+}$). L^8 forms a tetranuclear cyclic helicate upon reaction with Co^{2+} ([Co$_4$(L^8)$_4$]$^{8+}$) and in all cases the complexes are characterised by single-crystal X-ray diffraction and ESI-MS. The N-oxide units imparts flexibility in the ligand strand and where the unoxidised ligand strand forms a cyclic helicate, the incorporation of an N-oxide unit allows the formation of the dinuclear double helicate.

Introduction

To achieve the formation of metallosupramolecular architectures such as linear or circular helicates careful consideration has to go into ligand design.[1–6] These ligands must contain the correct number and arrangement of donor atoms such that not only the formation of the entropically favoured mononuclear assembly is prevented but the binding domains are sufficiently arranged so that a discrete self-assembled species (*e.g.* a dinuclear double helicate [M$_2$L$_2$]$^{2/4+}$ or cyclic helicates [M$_n$L$_n$]$^{2n+}$, where n = 3, 4, 5 *etc.*) is formed.[7] In a recent example, we showed that incorporation of a 1,3-phenylene spacer unit, within a potentially hexadentate ligand, can give different self-assembled species dependent upon the ionic radius of the metal ion used to coordinate the ligand strand. Reaction of L^1 with Cd^{2+} ions gives a relatively simple dinuclear double helicate [Cd$_2$(L^1)$_2$]$^{4+}$ whilst Zn^{2+} ions result in the assembly of a pentanuclear cyclic helicate [Zn$_5$(L^1)$_5$]$^{10+}$. This difference is attributed to the steric demands of the central phenyl unit. In the [Cd$_2$(L^1)$_2$]$^{4+}$ complex the distance between the two phenyl rings is *ca.* 4.2 Å and examination of the van der Waals radii reveals marginal surplus space between these inward facing protons. When smaller zinc ions are employed it is likely that any steric and/or electrostatic repulsion between

these protons would be significantly emphasized in an iso-structural dizinc(ii) helicate.[8]

This shows how the assembly of metallosupramolecular systems can be controlled by the correct positioning of metal binding domains and spacer units. In an analogous fashion the ligand L^2 which contains bidentate and tridentate domains separated by a 1,3-phenylene unit forms a penta-nuclear cyclic helicate with Cu^{2+} giving [Cu$_5$(L^2)$_5$]$^{10+}$ (Fig. 1).

In this structure the copper centre is coordinated by the bidentate tail of one ligand and a tridentate tail of a different ligand giving rise to a head-to-tail cyclic helicate.[8] There are a large number of self-assembled species resulting from the coordination of ligands containing many different donor units but surprisingly the use of the N-oxide donor unit has received little attention in self-assembly and its ability to control the formation of metallosupramolecular species has largely been overlooked. The only previously reported example incorporates N-oxide units within the middle of the ligand strand (L^3 and
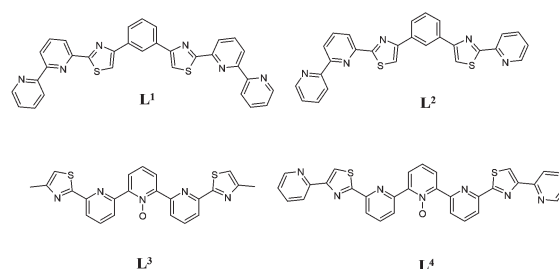
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Fig. 1 Ligands L^1–L^4.

L⁴) and this partitions the ligand into two separate binding domains with the N-oxide bridging the metal ion. Specifically, reaction of **L⁴** with Cd²⁺ gives a dinuclear double helicate with each of the Cd²⁺ ions coordinated by the N-oxide and pyridyl thiazole donor units of two different ligands giving the complex [Cd₂(**L⁴**)₂]⁴⁺.[9] Complexes of polydentate N-oxide ligands (*e.g.* 2,2′:6′,2″-terpyridine and 2,2′:6′,2″:6″,2‴-quaterpyridine) have been reported but these gave mononuclear species.[10]

In this work we demonstrate how an N-oxide unit can be incorporated into the terminal domains of the ligand strand and how this can affect the coordination ability of the ligand strand.

Experimental

Crystallographic details

Single crystal X-ray diffraction data were collected on a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(K$_\alpha$) radiation source and a cold stream of N₂ gas. In all examples the perchlorate or tetrafluoroborate counter ions contained varying degrees of disorder and were modelled in two positions using the part instruction and constrained using DELU and SIMU instructions in the least squares refinement. In the case of [Co₄(**L⁸**)₄]⁸⁺ the crystals lost solvent extremely rapidly and examination of the X-ray data showed that the complex contained diffuse solvent molecules and scattering contribution to these diffuse elements and electron density equating to two molecules of dichloromethane were removed using the Squeeze routine in Platon. These additional solvents are included in the moiety formula.

Crystal data for [Cu(**L⁵**)(ClO₄)₂(MeCN)][Cu(**L⁵**)(ClO₄)₂(H₂O)] (C₃₈H₂₉Cl₆Cu₂N₉O₂₇S₂): M = 1447.60, Triclinic, $P\bar{1}$, a = 9.4086(8), b = 16.9828(14), c = 18.2559(16) Å, α = 67.070(2), β = 82.993(2), γ = 74.439(2)°, V = 2587.5(4) Å³, Z = 2; ρ_{calc} = 1.858 Mg m⁻³, $F(000)$ = 1456; dimensions 0.35 × 0.3 × 0.1 mm³; $\mu(Mo_{K\alpha})$ = 1.314 mm⁻¹, T = 100 K. A total of 15 306 reflections were measured in the range 1.21 ≤ θ ≤ 26.02° (*hkl* range indices: −11 ≤ h ≤ 7, −20 ≤ k ≤ 20, −21 ≤ l ≤ 22), 10 037 unique reflections (R_{int} = 0.0645). The structure was refined on F^2 to R_w = 0.1326, R = 0.0581 (5604 reflections with $I > 2\sigma(I)$) and GOF = 0.986 on F^2 for 777 refined parameters, 25 restraints. Largest peak and hole 0.592 and −0.687 e Å⁻³. CCDC 918504.

Crystal data for [Ni₂(**L⁶**)₂](ClO₄)₄(MeNO₂)₅(H₂O) (C₅₅H₄₀Cl₄N₁₅Ni₂O₂₆S₄): M = 3384.92, Triclinic, $P\bar{1}$, a = 10.7357 (5), b = 13.4575(6), c = 23.2619(11) Å, α = 82.9930(10), β = 78.8390(10), γ = 82.3710(10)°, V = 3252.0(3) Å³, Z = 2; ρ_{calc} = 1.728 Mg m⁻³, $F(000)$ = 1719; dimensions 0.2 × 0.2 × 0.05 mm³; $\mu(Mo_{K\alpha})$ = 0.968 mm⁻¹, T = 150(2) K. A total of 57 654 reflections were measured in the range 1.70 ≤ θ ≤ 30.53° (*hkl* range indices: −15 ≤ h ≤ 15, −19 ≤ k ≤ 18, −33 ≤ l ≤ 33), 19 730 unique reflections (R_{int} = 0.0610). The structure was refined on F^2 to R_w = 0.1773, R = 0.0641 (11 017 reflections with $I > 2\sigma(I)$) and GOF = 1.036 on F^2 for 983 refined

parameters, 32 restraints. Largest peak and hole 1.180 and −0.903 e Å⁻³. CCDC 918505.

Crystal data for [Cu₂(**L⁷**)₂](ClO₄)₄(MeNO₂)₁.₁(CH₂Cl₂)₀.₆ (C₅₅.₃₈H₃₇.₈₃Cl₄.₆₀Cu₂N₁₁.₀₈O₂₀.₁₆S₄): M = 1599.26, Triclinic, $P\bar{1}$, a = 12.0799(12), b = 14.7340(15), c = 17.2067(17) Å, α = 95.609 (2), β = 94.864(2), γ = 90.453(2)°, V = 3036.5(5) Å³, Z = 2; ρ_{calc} = 1.749 Mg m⁻³, $F(000)$ = 1618.7; dimensions 0.9 × 0.5 × 0.1 mm³; $\mu(Mo_{K\alpha})$ = 1.129 mm⁻¹, T = 100(2) K. A total of 52 841 reflections were measured in the range 1.92 ≤ θ ≤ 27.88° (*hkl* range indices: −10 ≤ h ≤ 15, −19 ≤ k ≤ 19, −22 ≤ l ≤ 22), 14 250 unique reflections (R_{int} = 0.0400). The structure was refined on F^2 to R_w = 0.1232, R = 0.0453 (11 126 reflections with $I > 2\sigma(I)$) and GOF = 1.018 on F^2 for 978 refined parameters, 135 restraints. Largest peak and hole 1.630 and −1.276 e Å⁻³. CCDC 918503.

Crystal data for [Co₄(**L⁸**)₄](BF₄)₈(CH₂Cl₂)₈.₆(H₂O)₃(MeNO₂) (C₁₄₂.₆₅H₁₁₆.₃₁B₈Cl₁₉.₃₁Co₄F₃₂N₂₅O₁₇S₈): M = 4324.00, Triclinic, $P\bar{1}$, a = 17.9775(15), b = 21.8535(18), c = 24.415(2) Å, α = 105.483(2), β = 95.760(2), γ = 103.275(2)°, V = 8862.2(13) Å³, Z = 2; ρ_{calc} = 1.620 Mg m⁻³, $F(000)$ = 4351; dimensions 0.3 × 0.1 × 0.1 mm³; $\mu(Mo_{K\alpha})$ = 0.854 mm⁻¹, T = 150(2) K. A total of 164 320 reflections were measured in the range 1.52 ≤ θ ≤ 27.50° (*hkl* range indices: −23 ≤ h ≤ 23, −26 ≤ k ≤ 28, −29 ≤ l ≤ 31), 39 488 unique reflections (R_{int} = 0.0802). The structure was refined on F^2 to R_w = 0.1534, R = 0.0925 (21 115 reflections with $I > 2\sigma(I)$) and GOF = 1.084 on F^2 for 2357 refined parameters, 401 restraints. Largest peak and hole 2.625 and −1.169 e Å⁻³. CCDC 918502.

General details

Chemicals were purchased and used without further purification. ¹H NMR spectra were recorded on a 400 MHz Bruker Avance DPX400. Mass spectra were obtained on a Bruker MicroTOF-q LC mass spectrometer. Extreme care should be taken when using TMSCN and it should only be used in a well ventilated fume cupboard. The materials 2,2′-bipyridine-1,1′-bis-N-oxide, 2,2′-bipyridine-1-oxide, and 6-cyano-2,2′-bipyridine have all been prepared previously.[11]

Synthesis of 6′-cyano-2,2′-bipyridine-1-oxide (method 1). To a solution of 2,2′-bipyridine-*N*,*N*′dioxide (**1**) (0.20 g, 1.06 mmol) and benzoyl chloride (0.15 g, 1.06 mmol, 0.12 ml) in DCM (50 ml) was added trimethylsilyl cyanide (0.10 g, 1.06 mmol, 0.13 ml) and the reaction heated under reflux. The reaction was continually monitored by TLC (2% MeOH in DCM, Al₂O₃) until it was assumed that the maximum amount of mono-cyano compounds had formed (between four and six hours). The reaction was then cooled to room temperature, filtered and the solvent was reduced by rotary evaporation resulting in a viscous oil containing a mixture of both mono- and bis-cyano compounds and also any unreacted starting material. Purification of the crude product *via* column chromatography (Al₂O₃, 1% MeOH in DCM until the first fraction eluted, then 2% methanol in DCM,) gave (**2**) as a sandy solid (0.12 g, 0.61 mmol, 57%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 9.19 (dd, J = 8.3, 1.0, 1H), 8.25 (dd, J = 6.2, 1.0, 1H), 8.20 (dd, J = 8.1, 2.1, 1H), 7.91 (t, J = 7.7, 1H), 7.68 (dd, J = 7.7, 1.0, 1H),

7.35 (td, J = 7.7, 1.3, 1H), 7.28 (dt, J = 7.7, 2.2 Hz, 1H). ESI-MS m/z 220 (M + Na$^+$). HR ESI-MS found 220.0480 $C_{11}H_7N_3NaO$ requires 220.0481 (error = 0.46 ppm).

Synthesis of 6′-cyano-2,2′-bipyridine-1-oxide (method 2). To a solution of 6-cyano-2,2′-bipyridine (5) (0.20 g, 1.06 mmol) in DCM (25 ml) was slowly added, over a period of 2 hours, mCPBA (77%, 0.24 g, 1.06 mmol). After complete addition the reaction was allowed to stir for 8 h after which the solvent was evaporated and the resulting solid purified in an analogous fashion to method 1 (0.15 g, 0.76 mmol, 72%). The analytical data was identical to the product which was obtained from 2,2′-bipyridine-N,N'dioxide.

Synthesis of 1-N-oxide-2,2′-bipyridine-6′-thioamide. To a solution of the cyano compound (2) (0.70 g, 3.55 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol, 1.38 ml) was added and H$_2$S was slowly bubbled through the solution for 15 minutes, during which time the solution turned yellow. The yellow solution was allowed to stand for 48 hours during which time a yellow solid slowly precipitated. Collection via filtration gave pure (3) as a yellow solid (0.7 g, 3.03 mmol, 88% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.40 (s, 1H, NH), 8.97 (dd, J = 7.9, 0.80, 1H), 8.78 (dd, J = 7.9, 0.76, 1H), 8.36 (dd, J = 6.3, 0.80, 1H), 8.04 (dd, J = 8.0, 2.1, 1H), 8.00 (t, J = 7.9, 1H), 7.76 (s, 1H, NH), 7.41 (dt, J = 7.6, 1.2, 1H), 7.35 (dt, J = 6.6, 2.2 Hz, 1H). ESI-MS m/z 254 (M + Na$^+$). HR ESI-MS found 254.0371 $C_{11}H_9N_3NaOS$ requires 254.0359 (error −4.79 ppm).

Synthesis of 1,3-di(α-bromoacetyl)cresol. A solution of 1,3-diacetylcresol (0.50 g, 2.60 mmol) in acetic acid (20 ml) was heated to 80 °C after which time a solution of bromine (0.83 g, 0.27 ml, 5.20 mmol) in acetic acid (1 ml) was added drop-wise over a period of 1 hour. Once added the reaction was heated further for 30 minutes and then cooled to room temperature. The solvent was removed and the crude material was purified by column chromatography (SiO$_2$, 1% hexane in DCM) giving the dibromoacetyl species (9) as a light yellow solid (0.37 g, 1.05 mmol, 41%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 12.79 (s, 1H, −OH), 7.91 (s, 2H, Ar), 4.61 (s, 4H, −CH$_2$−), 2.40 (s, 3H, −CH$_3$). ESI-MS m/z 372 (M + Na$^+$). Hr ESI-MS found 370.8889 $C_{11}H_{10}Br_2NaO_3$ requires 370.8889 (error −0.07 ppm).

Synthesis of L^5. To a suspension of 1-N-oxide-2,2′-bipyridine-6′-thioamide (3) (0.1 g, 0.43 mmol) in EtOH (20 ml) was added 2-(α-bromoacetyl)-pyridinium hydrobromide (6) (0.14 g, 0.5 mmol) and the reaction refluxed for 8 hours, during which time all the reactants dissolved. The reaction was allowed to stand at room temperature for 12 hours and the resulting precipitate was filtered and washed with EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) and dried in $vacuo$ to give L^5·HBr. The hydrobromide salt was then suspended in aqueous ammonia (0.88 sp.gr., 5 ml) for 12 hours, filtered and washed with water (2 × 2 ml), EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) giving L^5 as a pale yellow solid (0.081 g, 0.24 mmol, 57%). ^{1}H NMR (400 MHz, d^6-DMSO) δ (ppm) 8.85 (d, J = 7.84, 1H, py), 8.67 (m, 1H, py), 8.47 (s, 1H, tz), 8.44 (d, J = 5.64, 1H), 8.35 (d, J = 7.8, 1H, py), 8.26–8.15 (m, overlapping, 3H), 7.98 (t, J = 7.6 Hz, 1H, py), 7.57–7.56 (m, overlapping, 2H), 7.42 (m, 1H, py).

ESI-MS m/z 333 (M + H$^+$). Found: C, 64.7; H, 3.8; N, 16.5%; $C_{18}H_{12}N_4OS$ requires C, 65.0; H, 3.6; N, 16.9%.

Synthesis of L^6. To a suspension of 1-N-oxide-2,2′-bipyridine-6′-thioamide (3) (0.1 g, 0.43 mmol) in EtOH (20 ml) was added 1,4-dibromo-2,3-dione (7) (0.05 g, 0.20 mmol) and the reaction refluxed for 8 hours. The reaction was allowed to cool and the precipitate was filtered and washed with EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) and dried in $vacuo$ to give L^6·HBr. The hydrobromide salt was then suspended in aqueous ammonia (0.88 sp.gr., 5 ml) for 12 hours, filtered and washed with water (2 × 2 ml), EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) giving L^6 as a pale yellow solid (0.08 g, 0.16 mmol, 74%). ESI-MS m/z 509 (M + H$^+$). The solubility of the ligand was very poor, even in d^6-DMSO at 80 °C and precluded ^{1}H NMR analysis. Found: C, 61.6; H, 3.5; N, 16.0%; $C_{26}H_{16}N_6O_2S_2$ requires C, 61.4; H, 3.2; N, 16.5%.

Synthesis of L^7. To a suspension of 1-N-oxide-2,2′-bipyridine-6′-thioamide (3) (0.1 g, 0.43 mmol) in EtOH (20 ml) was added the thiazole-containing α-bromoacetyl (8) (0.15 g, 0.42 mmol) and the reaction refluxed for 8 hours, during which time all the reactants dissolved. The reaction was allowed to stand at room temperature for 12 hours and the resulting precipitate was filtered and washed with EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) and dried in $vacuo$ to give L^7·HBr. The hydrobromide salt was then suspended in aqueous ammonia (0.88 sp.gr., 5 ml) for 12 hours, filtered and washed with water (2 × 2 ml), EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) giving L^7 as a pale yellow solid (0.11 g, 52%). ^{1}H NMR (500 MHz, d^6-DMSO) δ (ppm) 8.86 (d, J = 7.87, 1H, py), 8.75 (t, J = 0.8, 1H, Ph), 8.67 (m, 1H, py), 8.49 (s, 1H, tz), 8.42–8.46 (m, overlapping, 3H), 8.34 (d, J = 7.8, 1H, py), 8.24 (dd, J = 9.0, 2.4, 1H, py), 8.18 (t, J = 7.8, 1H, py), 8.13–8.09 (m, overlapping, 2H, Ph), 8.04 (dt, J = 7.7, 1.6, 1H, py), 7.63 (t, J = 7.6 Hz, 1H, Ph), 7.60–7.55 (m, overlapping, 3H, py). ESI-MS m/z 492 (M + H$^+$). Found: C, 66.4; H, 3.6; N, 13.9%; $C_{27}H_{17}N_5OS_2$ requires C, 66.0; H, 3.5; N, 14.2%.

Synthesis of L^8. To a suspension of 1-N-oxide-2,2′-bipyridine-6′-thioamide (3) (0.1 g, 0.43 mmol) in dimethylformamide (10 ml) was added 1,3-di(α-bromoacetyl)cresol (9) (0.068 g, 0.19 mmol) and the reaction heated at 80 °C for 8 hours. The reaction was allowed to cool and the precipitate was filtered and washed with EtOH (4 × 2 ml) and Et$_2$O (2 × 2 ml) and dried in $vacuo$ to give L^8·HBr. The hydrobromide salt was then suspended in aqueous ammonia (0.88 sp.gr., 5 ml) for 12 hours, filtered and washed with water (2 × 2 ml), EtOH (2 × 2 ml) and Et$_2$O (2 × 2 ml) giving L^8 as a pale yellow solid (0.065 g, 49%). As with L^6 the solubility of the ligand was very poor, even in d^6-DMSO at 80 °C and precluded ^{1}H NMR analysis. ESI-MS m/z 616 (M + H$^+$). Found: C, 64.8; H, 3.9; N, 13.2%; $C_{33}H_{22}N_6O_3S_2$ requires C, 64.5; H, 3.6; N, 13.7%.

In all cases the complexes were synthesized in a similar manner and the ligand (5 mg) was reacted with 1.1 equivalents of the relevant metal ion in MeCN (L^5) or MeNO$_2$ (L^6–L^8) and the reaction heated and sonicated until complete dissolution. Slow diffusion of dichloromethane ([Cu$_2$(L^7)$_2$](ClO$_4$)$_4$ and [Co$_4$(L^8)$_4$](BF$_4$)$_8$), diethyl ether (Cu(L^5)(ClO$_4$)$_2$) and ethyl acetate

([Ni$_2$(L^6)$_2$](ClO$_4$)$_4$) gave crystalline materials which were isolated by filtration, washed with the diffusion solvent and dried under vacuum. [Cu(L^5)(ClO$_4$)$_2$(MeCN)][Cu(L^5)(ClO$_4$)$_2$(H$_2$O)] (yield = 43%). Found: C, 36.4; H, 2.6; N, 9.8. Calculated for C$_{38}$H$_{29}$N$_9$O$_{19}$S$_2$Cu$_2$Cl$_4$: C, 36.6; H, 2.3; N, 10.1%. [Ni$_2$(L^6)$_2$]-(ClO$_4$)$_4$ (yield = 65%) Found: C, 40.4; H, 1.8; N, 10.8%. Calculated for C$_{52}$H$_{32}$N$_{12}$O$_{20}$S$_4$Ni$_2$Cl$_4$: C, 40.8; H, 2.1; N, 11.0%. [Cu$_2$(L^7)$_2$](ClO$_4$)$_4$ (yield = 53%) Found: C, 42.8; H, 2.4; N, 9.1%. Calculated for C$_{54}$H$_{34}$N$_{10}$O$_{18}$S$_4$Cu$_2$Cl$_4$: C, 43.0; H, 2.3; N, 9.3%. [Co$_4$(L^8)$_4$](BF$_4$)$_8$ (yield = 47%) Found: C, 44.8; H, 2.2; N, 9.1%. Calculated for C$_{132}$H$_{88}$N$_{24}$O$_{12}$S$_8$Co$_4$B$_8$F$_{32}$·C$_2$H$_4$Cl$_4$: C, 45.2; H, 2.6; N, 9.5%.

Results and discussion

Ligand synthesis

The principal material for the formation of these N-oxide ligands is 6′-cyano-2,2′-bipyridine-1-oxide (2) which can be prepared *via* two different routes. The first route involves the reaction of 2,2′-bipyridine-bis-1,1′-oxide (1) with benzoyl chloride and tetramethylsilylcyanide in dichloromethane; the reaction monitored by TLC until it was judged that the maximum quantity of 6′-cyano-2,2′-bipyridine-1-oxide (2) had formed. Alternatively, 6′-cyano-2,2′-bipyridine-1-oxide can be prepared by reaction 2,2′-bipyridine-1-oxide (4) with TMSCN to give 6-cyano-2,2′-bipyridine (5) and then reaction with *m*CPBA which gives 6′-cyano-2,2′-bipyridine-1-oxide (2), the selectivity in oxidation presumably controlled by the electronic and steric effects of the cyano group (Scheme 1). Although the second route requires more synthetic steps we found it the most reliable method of preparation as the yields starting from 2,2′-bipyridine-bis-1,1′-oxide were variable. Reaction of the thioamide (3) with α-bromoacetyls (6)–(9) either in EtOH or DMF followed by deprotonation with concentrated ammonia gave the corresponding ligands L^5–L^8 (Scheme 2).

Coordination chemistry

Reaction of ligand L^5 with Cu(ClO$_4$)$_2$·6H$_2$O. Reaction of L^5 with Cu(ClO$_4$)$_2$·6H$_2$O in MeCN gave a green solution from which crystals were obtained by slow diffusion of ethyl acetate.
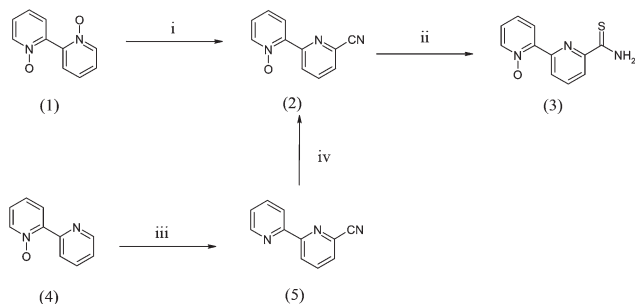
Scheme 1 Synthesis of 6′-cyano-2,2′-bipyridine-1-oxide. Reagents and conditions: (i) TMSCN, BzCl, CH$_2$Cl$_2$, reflux; (ii) H$_2$S, Et$_3$N, EtOH, RT; (iii) TMSCN, BzCl, CH$_2$Cl$_2$, reflux; (iv) *m*CPBA, CH$_2$Cl$_2$, RT.
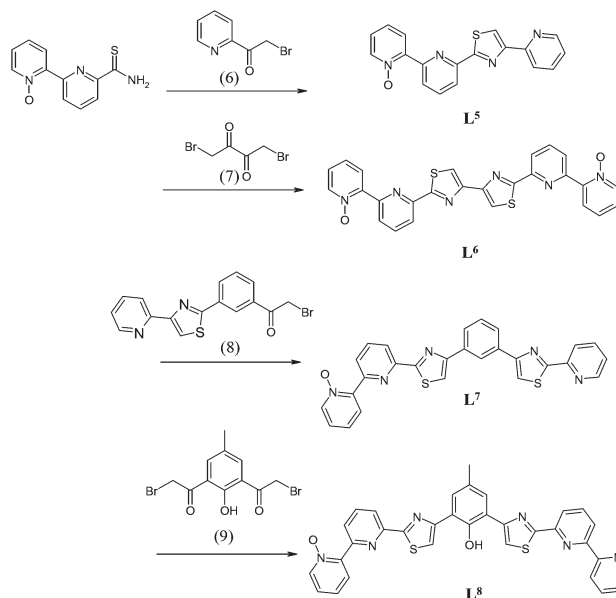
Scheme 2 Synthesis of ligands L^5–L^8.
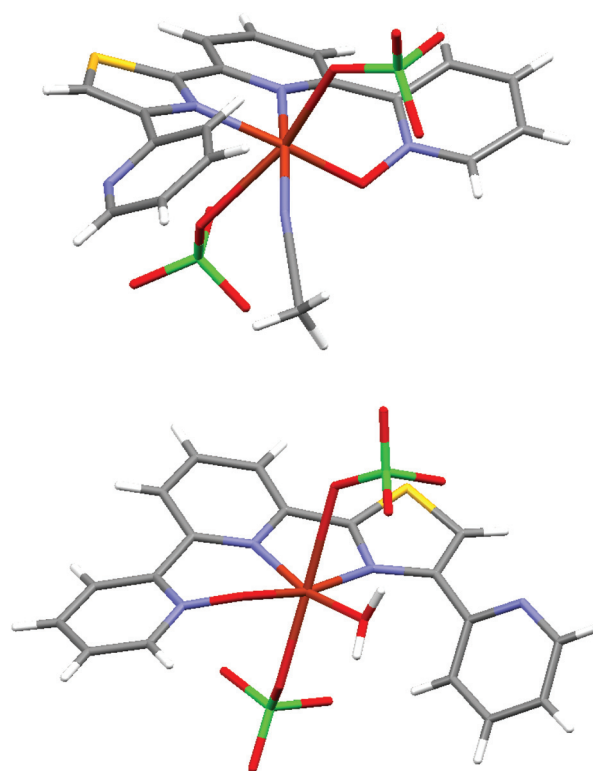
Fig. 2 X-ray crystal structure of [Cu(L^5)(ClO$_4$)$_2$(MeCN)] (top) and [Cu(L^5)-(ClO$_4$)$_2$(H$_2$O)] (bottom).

In the solid state there are two different molecules in the unit cell, each of which contains a 6-coordinate metal centre formed by coordination of one ligand strand, two perchlorate counter ions and either a water molecule or a molecule of acetonitrile giving the simple mononuclear species [Cu(L^5)-(ClO$_4$)$_2$(sol)] where sol = H$_2$O or MeCN (Fig. 2) (Cu–N:

1.96–2.03 Å; Cu–ON: 1.92 Å). In both cases the ligand acts as a tridentate donor, coordinating the metal centre by thiazole and pyridine N-donor units and the terminal O-donor N-oxide. The terminal N-donor unit does not coordinate the metal centre which can be attributed to the divergent nature of the pyridyl-thiazole-pyridyl domains which prevents the ligand acting as a tetradentate chelate.

In the ESI-MS an ion is observed at $m/z = 494$ which corresponds to $\{[Cu(\mathbf{L^5})]ClO_4\}^+$, however higher molecular weight ions at $m/z = 1088, 1683, 2280$ and 2873 which correspond to $\{[Cu_n(\mathbf{L^5})_n](ClO_4)_{2n-1}\}^+$, where $n = 2, 3, 4$ and 5 are also observed. It is likely that these higher nuclearity ions are due to aggregation of the mononuclear species during the ESI-MS process.

Reaction of ligand $\mathbf{L^6}$ with Ni(ClO$_4$)$_2$·6H$_2$O. Reaction of ligand $\mathbf{L^6}$ with Ni(ClO$_4$)$_2$·6H$_2$O in MeNO$_2$ gives a green solution from which light green crystals are produced after slow diffusion of tetrahydrofuran. ESI-MS analysis gave a remarkably simple spectrum with ions at $m/z = 1433, 922$ and 665 corresponding to $\{[Ni_2(\mathbf{L^6})_2](ClO_4)_3\}^+$, $\{[Ni_2(\mathbf{L^6})](ClO_4)_3\}^+$ and $\{[Ni_2(\mathbf{L^6})_2](ClO_4)_2\}^{2+}$. Solid-state analysis shows the formation of a dinuclear double helicate $[Ni_2(\mathbf{L^6})_2]^{4+}$; each of the ligand strands partitions into two tridentate domains comprising thiazole-pyridyl-pyridyl-N-oxide donor units (Fig. 3). Each of the Ni^{2+} ions adopts a six-coordinate geometry and is coordinated by two tridentate domains from different ligands (Ni–N: 2.04–2.05 Å; Ni–O: 2.02–2.05 Å).

Reaction of ligand $\mathbf{L^7}$ with Cu(ClO$_4$)$_2$·6H$_2$O. Reaction of ligand $\mathbf{L^7}$ with Cu(ClO$_4$)$_2$·6H$_2$O in MeNO$_2$ gives a green solution from which green crystals were produced upon slow diffusion of CH$_2$Cl$_2$. As with the Ni^{2+} complex, the ESI-MS analysis was straightforward with ions at $m/z = 1407$ and 915 corresponding to $\{[Cu_2(\mathbf{L^7})_2](ClO_4)_3\}^+$ and $\{[Cu_2(\mathbf{L^7})](ClO_4)_3\}^+$. Solid-state analysis shows the formation of a head-to-tail dinuclear double helicate $[Cu_2(\mathbf{L^7})_2]^{4+}$ where the ligand partitions into a tridentate and a bidentate domain separated by a 1,3-phenylene spacer (Fig. 4). Each of the Cu^{2+} ions is coordinated by N-oxide-pyridyl-thiazole unit from one ligand and a pyridyl-thiazole unit from a different ligand giving a 5-coordinate metal centre (Cu–N: 1.98–2.43 Å; Cu–O: 1.96 Å). It is somewhat surprising that this ligand gives a dinuclear double helicate with Cu^{2+} as we have previously shown that this type of ligand (i.e. containing a 1,3-phenylene spacer) usually produces a pentanuclear cyclic helicate upon coordination with first-row transition metal ions. These cyclic helicates result due to unfavourable steric interactions between the spacer units. However, the inclusion of an N-oxide must allow the ligand to flex so that the two phenyl units are more remote, reducing the steric interaction. Indeed, the distance between the phenyl carbon atoms is 4.2 Å (cf. $[Cd_2(\mathbf{L^1})_2]^{4+}$ inter-ligand phenyl separation 4.2 Å).

Reaction of ligand $\mathbf{L^8}$ with Co(BF$_4$)$_2$·6H$_2$O. Ligand $\mathbf{L^8}$ contains two thiazole-pyridyl-pyridyl-N-oxide donor units separated by a 1,3-phenol spacer. Upon reaction of this ligand with Co(BF$_4$)$_2$·6H$_2$O a pale orange solution results from which crystals were produced upon slow diffusion of dichloromethane.
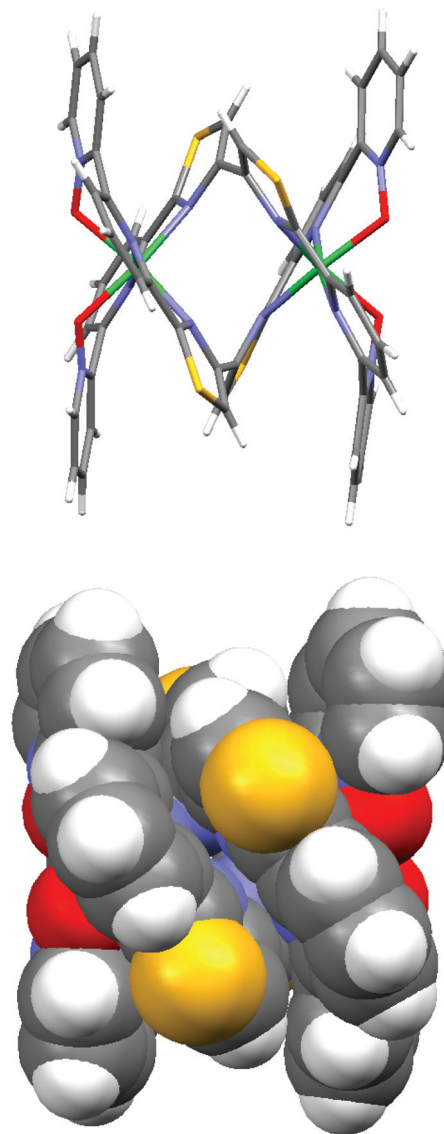

Fig. 3 X-ray crystal structure of $[Ni_2(\mathbf{L^6})_2]^{4+}$ (top) and as a space-filling model (bottom).

Solid state analysis shows the formation of a tetranuclear cyclic helicate $[Co_4(\mathbf{L^8})_4]^{8+}$, where each of the ligands has separated into tridentate thiazole-pyridyl-pyridyl-N-oxide donor units separated by a 1,3-phenol unit (Fig. 5). All four cobalt ions are six-coordinate arising from the coordination of two of the N, N, O-donor units (Co–N: 2.11–2.20 Å; Co–O: 2.00–2.07 Å). The phenol spacers bridge each of the domains in an "over and under" conformation, giving rise to a helical cyclic oligomer. The four –OH units do not coordinate to the metal centres but hydrogen bond to one another.

Interestingly, analogous complexes that contain ligands with a 1,3-phenyl spacer unit give *pentanuclear* cyclic helicates, whereas with a 1,3-phenol spacer the lower *tetranuclear* species is observed. It seems likely that this can be attributed to the steric bulk of the methyl group on the central phenol spacer. In a tetranuclear assembly the distance between adjacent
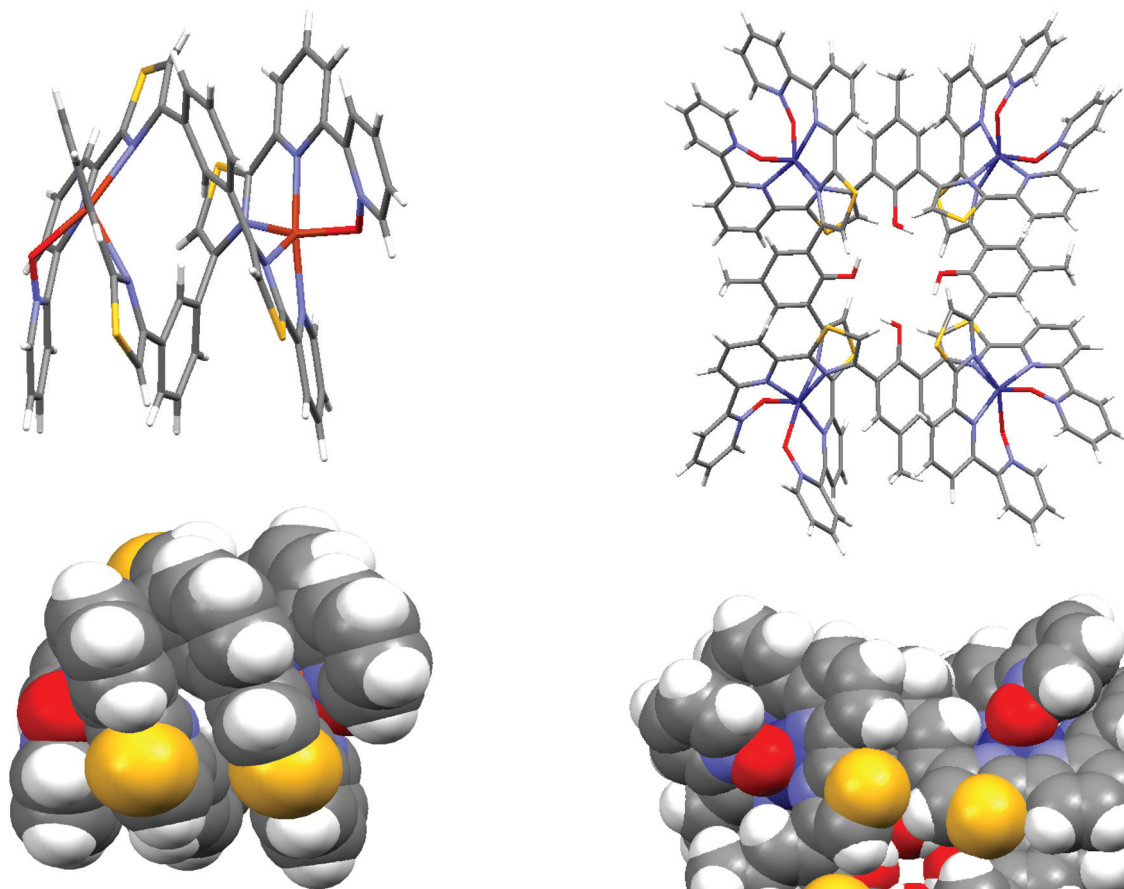
Fig. 4 X-ray crystal structure of $[Cu_2(L^7)_2]^{4+}$ (top) and as a space-filling model (bottom).

Fig. 5 X-ray crystals structure of $[Co_4(L^8)_4]^{8+}$ (top) and as a space-filling model (bottom).

tridentate binding domains will be longer than the corresponding pentanuclear cyclic helicate and the steric demands of the methyl groups will thus prevent the pentanuclear assembly. Measurement of the centriods of the central pyridine rings in adjacent ligand strands show that the distance is substantially longer in $[Co_4(L^8)_4]^{8+}$ (~8.0 Å) than the pentanuclear species $[Zn_5(L^1)_5]^{10+}$ (~7.0 Å). ESI-MS shows a doubly charged ion at $m/z = 1607$ corresponding to the tetranuclear cyclic helicate $\{[Co_4(L^8)_4](ClO_4)_6\}^{2+}$. Also an ion at $m/z = 2454$ corresponding to $\{[Co_3(L^8)_3](ClO_4)_5\}^+$ was observed, the presence of this the lower nuclearity species is probably an artefact of the ESI-MS process and has been observed in other cyclic helicate systems.[8] Whereas with L^7 the N-oxide units allow the ligand to flex and form the double helicate, here the steric bulk of the –OH unit is sufficiently large that even with the added flexibility that the N-oxide unit imparts a double helicate cannot be formed.

Conclusions

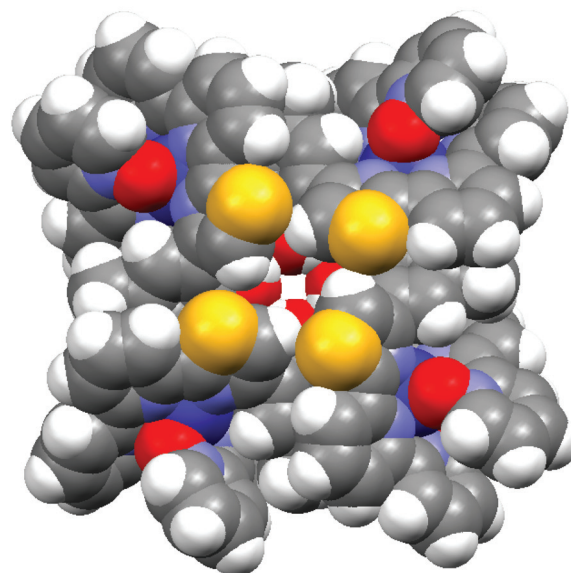We have developed a method that allows incorporation of N-oxide units as the terminal donor units in a series of polydentate ligands which produce, upon coordination with different d-block metal ions, a mononuclear single stranded complex as well as a dinuclear double stranded and tetranuclear circular helicates. The incorporation of this unit within the ligand strand can change the behaviour of the ligand as it increases the flexibility of the donor units. How the ligand would behave with other metal ions is unknown. However, we have found that for the most part, ligands that can partition into two tridentate domains, give similar results with all the divalent 1st row transition metal ions.[3,6,8,11] For example, reaction of L^6 with other metals such as Co^{2+}, Fe^{2+} or Zn^{2+} would all give the dinuclear double helicate species $[M_2(L^6)_2]^{4+}$ however despite attempts we cannot obtain crystals of sufficient quality to confirm this.

Acknowledgements

Notes and references

1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley and Sons, Chichester, 2000; M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2004, 167; M. Albrecht, *Chem. Rev.*, 2001, **101**, 3547; M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281; C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; E. C. Constable, in *Comprehensive Supramolecular Chemistry, vol. 9; Polynuclear Transition Metal Helicates*, ed. J.-P. Sauvage, Elsevier, Oxford, 1996, p. 213.

2 A. Stephenson and M. D. Ward, *Chem. Commun.*, 2012, 3605.

3 C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *Chem. Commun.*, 2000, 1529; C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2001, 550.

4 E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1669; E. C. Constable, S. M. Elder, J. Healy, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 4590.

5 E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1996, 2423.

6 C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2001, 550; T. Riis-Johannessen, L. P. Harding, J. C. Jeffery, A. P. Robson and C. R. Rice, *Inorg. Chim. Acta*, 2005, **358**, 2781; C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *Chem. Commun.*, 2000, 1529.

7 L. J. Childs, M. Pascu, A. J. Clarke, N. W. Alcock and M. J. Hannon, *Chem.–Eur. J.*, 2004, **10**, 4291; L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2002, **41**, 4244; G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1999, 195; B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize and A. Van Dorsselaer, *Angew. Chem., Int. Ed.*, 1998, **37**, 3265; J. Hamblin, F. Tuna, S. Bunce, L. J. Childs, A. Jackson, W. Errington, N. W. Alcock, H. Nierengarten, A. V. Dorsselaer, E. Leize-Wagner and M. J. Hannon, *Chem.–Eur. J.*, 2007, **13**, 9286; J. F. Ayme, J. E. Beves, D. A. Leigh, R. T. McBurney, K. Rissanen and D. Schultz, *J. Am. Chem. Soc.*, 2012, **134**, 9488; Z. S. Wu, J. T. Hsu, C. C. Hsieh and Y. C. Horng, *Chem. Commun.*, 2012, 3436.

8 L. Bain, S. Bullock, L. P. Harding, T. Riis-Johannessen, G. Midgley, C. R. Rice and M. Whitehead, *Chem. Commun.*, 2010, 3496; K. E. Allen, R. A. Faulkner, L. P. Harding, C. R. Rice, T. Riis-Johannessen, M. L. Voss and M. Whitehead, *Angew. Chem., Int. Ed.*, 2010, 6655; O. R. Clegg, R. V. Fennessy, L. P. Harding, C. R. Rice, T. Riis-Johannessen and N. C. Fletcher, *Dalton Trans.*, 2011, 12381.

9 G. Bokolinis, J. C. Jeffery, T. Riis-Johannessen and C. R. Rice, *New J. Chem.*, 2008, **32**, 115–119.

10 A. J. Amoroso, M. W. Burrows, T. Gelbrich, R. Haigh and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 2002, 2415; A. J. Amoroso, M. W. Burrows, A. A. Dickinson, C. Jones, D. J. Willock and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 2001, 255.

11 T. Riis-Johannessen, L. P. Harding, J. C. Jeffery, R. Moon and C. R. Rice, *Dalton Trans.*, 2007, 1577; T. Riis-Johannessen, J. C. Jeffery, A. P. H. Robson, C. R. Rice and L. P. Harding, *Inorg. Chim. Acta*, 2005, **358**, 2781.