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Bullock, Samantha, Harding, Lindsay P., Moore, Michelle, Mills, Andrew, Piela, Sean A.F., Rice, Craig R., Towns-Andrews, Elizabeth and Whitehead, Martina

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ARTICLE TYPE

# Synthesis of Ligands Containing N-oxide Donor Atoms and Their Assembly into Metallosupramolecular Structures.

Samantha Bullock,<sup>a</sup> Lindsay P. Harding,<sup>a</sup> Michelle Moore,<sup>a</sup> Andrew Mills,<sup>a</sup> Sean A. F. Piela,<sup>a</sup> Craig R. Rice,<sup>a\*</sup> Liz Towns-Andrews,<sup>a\*</sup> and Martina Whitehead.<sup>a</sup>

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A series of ligands that contain both N-donor and N-oxide donor atoms have been synthesised and ligands **L**<sup>5</sup>, **L**<sup>6</sup>, **L**<sup>7</sup> and **L**<sup>8</sup> contain, 4, 6, 5, and 6 donor atoms respectively. The smallest ligand **L**<sup>5</sup> forms a mononuclear complex with Cu<sup>2+</sup> ([Cu(**L**<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(MeCN)] whereas **L**<sup>6</sup> and **L**<sup>7</sup> form dinuclear double  
10 helicates with Ni<sup>2+</sup> and Cu<sup>2+</sup> respectively ([Ni<sub>2</sub>(**L**<sup>6</sup>)<sub>2</sub>]<sup>4+</sup> and [Cu<sub>2</sub>(**L**<sup>7</sup>)<sub>2</sub>]<sup>4+</sup>). **L**<sup>8</sup> forms a tetranuclear cyclic helicate upon reaction with Co<sup>2+</sup> ([Co<sub>4</sub>(**L**<sup>8</sup>)<sub>4</sub>]<sup>8+</sup>) 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.

## 15 Introduction

To achieve the formation of metallosupramolecular architectures such as linear or circular helicates careful consideration has to go into ligand design.<sup>1-6</sup> These ligands must contain the correct number and arrangement of donor atoms such that not only the  
20 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<sub>2</sub>L<sub>2</sub>]<sup>2+/4+</sup> or cyclic helicates [M<sub>n</sub>L<sub>n</sub>]<sup>2n+</sup>, where n = 3, 4, 5 etc) is formed.<sup>7</sup> In a recent example, we showed that  
25 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**<sup>1</sup> with Cd<sup>2+</sup> ions gives a relatively simple dinuclear double helicate [Cd<sub>2</sub>(**L**<sup>1</sup>)<sub>2</sub>]<sup>4+</sup> whilst  
30 Zn<sup>2+</sup> ions result in the assembly of a pentanuclear cyclic helicate [Zn<sub>5</sub>(**L**<sup>1</sup>)<sub>5</sub>]<sup>10+</sup>. This difference is attributed to the steric demands of the central phenyl unit. In the [Cd<sub>2</sub>(**L**<sup>1</sup>)<sub>2</sub>]<sup>4+</sup> complex the distance between the two phenyl rings is *ca.* 4.2 Å and examination of the van der Waals radii reveals marginal surplus  
35 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 isostructural dizinc(II) helicate.<sup>8</sup>

This shows how the assembly of metallosupramolecular systems  
40 can be controlled by the correct positioning of metal binding domains and spacer units. In an analogous fashion the ligand **L**<sup>2</sup> which contains bidentate and tridentate domains separated by a 1,3-phenylene unit forms a pentanuclear cyclic helicate with Cu<sup>2+</sup> giving [Cu<sub>5</sub>(**L**<sup>2</sup>)<sub>5</sub>]<sup>10+</sup>.

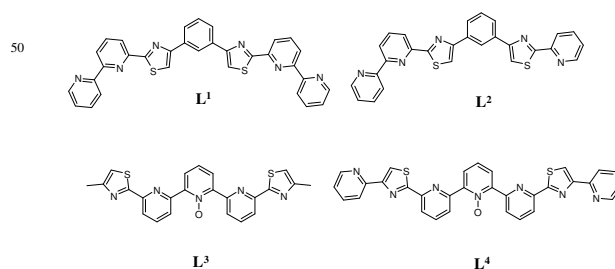


Fig. 1 Ligands **L**<sup>1</sup> – **L**<sup>4</sup>.

In this structure the copper centre is coordinated by the bidentate tail of one ligand and a tridentate tail of a different ligand giving  
60 rise to a head-to-tail cyclic helicate.<sup>8</sup> 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  
65 metallosupramolecular species has largely been overlooked. The only previously reported example incorporates N-oxide units within the middle of the ligand strand (**L**<sup>3</sup> and **L**<sup>4</sup>) and this partitions the ligand into two separate binding domains with the N-oxide bridging the metal ion. Specifically, reaction of **L**<sup>4</sup> with  
70 Cd<sup>2+</sup> gives a dinuclear double helicate with each of the Cd<sup>2+</sup> ions coordinated by the N-oxide and pyridyl thiazole donor units of two different ligands giving the complex [Cd<sub>2</sub>(**L**<sup>4</sup>)<sub>2</sub>]<sup>4+</sup>.<sup>9</sup> Complexes of polydentate N-oxide ligands (e.g. 2,2':6',2''-terpyridine and 2,2':6',2''':6''',2''''-quaterpyridine) have been  
75 reported but these gave mononuclear species.<sup>10</sup>

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.

## 5 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 N $_2$  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 [Co $_4$ (L $^8$ ) $_4$ ] $^{8+}$  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(L $^5$ )(ClO $_4$ ) $_2$ (MeCN)][Cu(L $^5$ )(ClO $_4$ ) $_2$ (H $_2$ O)] (C $_{38}$ H $_{29}$ Cl $_6$ Cu $_2$ N $_9$ O $_{27}$ S $_2$ ): M = 1447.60, Triclinic, P-1, a = 9.4086 (8), b = 16.9828 (14), c = 18.2559 (16) Å,  $\alpha$  = 67.070(2),  $\beta$  = 82.993(2),  $\gamma$  = 74.439(2)°, V = 2587.5 (4) Å $^3$ , Z = 2;  $\rho_{\text{calc}}$  = 1.858 Mg m $^{-3}$ , F(000) = 1456; dimensions 0.35×0.3×0.1 mm $^3$ ;  $\mu(\text{MoK}\alpha)$  = 1.314 mm $^{-1}$ , T = 100 K. A total of 15306 reflections were measured in the range 1.21 ≤  $\theta$  ≤ 26.02° (*hkl* range indices: -11 ≤ *h* ≤ 7, -20 ≤ *k* ≤ 20, -21 ≤ *l* ≤ 22), 10037 unique reflections (R $_{\text{int}}$  = 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 eÅ $^{-3}$ . CCDC 918504.

Crystal data for [Ni $_2$ (L $^6$ ) $_2$ ](ClO $_4$ ) $_4$ (MeNO $_2$ ) $_5$ (H $_2$ O)] (C $_{55}$ H $_{40}$ Cl $_4$ N $_{15}$ Ni $_2$ O $_{26}$ S $_4$ ): M = 3384.92, Triclinic, P-1, a = 10.7357(5), b = 13.4575(6), c = 23.2619(11) Å,  $\alpha$  = 82.9930(10),  $\beta$  = 78.8390(10),  $\gamma$  = 82.3710(10)°, V = 3252.0(3) Å $^3$ , Z = 2;  $\rho_{\text{calc}}$  = 1.728 Mg m $^{-3}$ , F(000) = 1719; dimensions 0.2×0.2×0.05 mm $^3$ ;  $\mu(\text{MoK}\alpha)$  = 0.968 mm $^{-1}$ , T = 150(2) K. A total of 57654 reflections were measured in the range 1.70 ≤  $\theta$  ≤ 30.53° (*hkl* range indices: -15 ≤ *h* ≤ 15, -19 ≤ *k* ≤ 18, -33 ≤ *l* ≤ 33), 19730 unique reflections (R $_{\text{int}}$  = 0.0610). The structure was refined on F $^2$  to R $_w$  = 0.1773, R = 0.0641 (11017 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 eÅ $^{-3}$ . CCDC 918505.

Crystal data for [Cu $_2$ (L $^7$ ) $_2$ ](ClO $_4$ ) $_4$ (MeNO $_2$ ) $_{1.1}$ (CH $_2$ Cl $_2$ ) $_{0.6}$  (C $_{55.38}$ H $_{37.83}$ Cl $_{4.60}$ Cu $_2$ N $_{11.08}$ O $_{20.16}$ S $_4$ ): M = 1599.26, Triclinic, P-1, a = 12.0799(12), b = 14.7340(15), c = 17.2067(17) Å,  $\alpha$  = 95.609(2),  $\beta$  = 94.864(2),  $\gamma$  = 90.453(2)°, V = 3036.5(5) Å $^3$ , Z = 2;  $\rho_{\text{calc}}$  = 1.749 Mg m $^{-3}$ , F(000) = 1618.7; dimensions 0.9×0.5×0.1 mm $^3$ ;  $\mu(\text{MoK}\alpha)$  = 1.129 mm $^{-1}$ , T = 100(2) K. A total of 52841 reflections were measured in the range 1.92 ≤  $\theta$  ≤ 27.88° (*hkl* range indices: -10 ≤ *h* ≤ 15, -19 ≤ *k* ≤ 19, -22 ≤ *l* ≤ 22), 14250 unique reflections (R $_{\text{int}}$  = 0.0400). The structure was refined on F $^2$  to R $_w$  = 0.1232, R = 0.0453 (11126 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 eÅ $^{-3}$ . CCDC 918503.

Crystal data for [Co $_4$ (L $^8$ ) $_4$ ](BF $_4$ ) $_8$ (CH $_2$ Cl $_2$ ) $_{8.6}$ (H $_2$ O) $_3$ (MeNO $_2$ ) $_6$  (C $_{142.65}$ H $_{116.31}$ B $_8$ Cl $_{19.31}$ Co $_4$ F $_{32}$ N $_{25}$ O $_{17}$ S $_8$ ): M = 4324.00, Triclinic, P-1, a = 17.9775(15), b = 21.8535(18), c = 24.415(2) Å,  $\alpha$  = 105.483(2),  $\beta$  = 95.760(2),  $\gamma$  = 103.275(2)°, V = 8862.2(13) Å $^3$ , Z = 2;  $\rho_{\text{calc}}$  = 1.620 Mg m $^{-3}$ , F(000) = 4351; dimensions 0.3×0.1×0.1 mm $^3$ ;  $\mu(\text{MoK}\alpha)$  = 0.854 mm $^{-1}$ , T = 150(2) K. A total of 164320 reflections were measured in the range 1.52 ≤  $\theta$  ≤ 27.50° (*hkl* range indices: -23 ≤ *h* ≤ 23, -26 ≤ *k* ≤ 28, -29 ≤ *l* ≤ 31), 39488 unique reflections (R $_{\text{int}}$  = 0.0802). The structure was refined on F $^2$  to R $_w$  = 0.1534, R = 0.0925 (21115 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 eÅ $^{-3}$ . CCDC 918502.

### General details

Chemicals were purchased and used without further purification.  $^1\text{H}$  NMR spectra were recorded on a 400MHz 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.<sup>11</sup>

**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, Al $_2$ O $_3$ ) 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 (Al $_2$ O $_3$ , 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%).  $^1\text{H}$  NMR (500 MHz, CDCl $_3$ )  $\delta$  (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 $_7$ N $_3$ NaO 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 hrs 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). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). HR ESI-MS found 254.0371 C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>NaOS 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<sub>2</sub>, 1% hexane in DCM) giving the dibromoacetyl species (**9**) as a light yellow solid (0.37 g, 1.05 mmol, 41%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 12.79 (s, 1H, -OH), 7.91 (s, 2H, Ar), 4.61 (s, 4H, -CH<sub>2</sub>-), 2.40 (s, 3H, -CH<sub>3</sub>). ESI-MS *m/z* 372 (M + Na<sup>+</sup>). Hr ESI-MS found 370.8889 C<sub>11</sub>H<sub>10</sub>Br<sub>2</sub>NaO<sub>3</sub> requires 370.8889 (error -0.07 ppm).

**Synthesis of L<sup>5</sup>.** 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 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) and dried *in vacuo* to give L<sup>5</sup>•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 x 2 ml), EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) giving L<sup>5</sup> as a pale yellow solid (0.081 g, 0.24 mmol, 57 %). <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-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<sup>+</sup>). Found: C, 64.7; H, 3.8; N, 16.5%; C<sub>18</sub>H<sub>12</sub>N<sub>4</sub>OS requires C, 65.0; H, 3.6; N, 16.9%.

**Synthesis of L<sup>6</sup>.** 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 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) and dried *in vacuo* to give L<sup>6</sup>•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 x 2 ml), EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) giving L<sup>6</sup> as a pale yellow solid (0.08 g, 0.16 mmol, 74 %). ESI-MS *m/z* 509 (M + H<sup>+</sup>). The solubility of the ligand was very poor, even in d<sup>6</sup>-DMSO at 80 °C and precluded <sup>1</sup>H NMR analysis. Found: C, 61.6; H, 3.5; N, 16.0%; C<sub>26</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub> requires C, 61.4; H, 3.2; N, 16.5%.

**Synthesis of L<sup>7</sup>.** 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

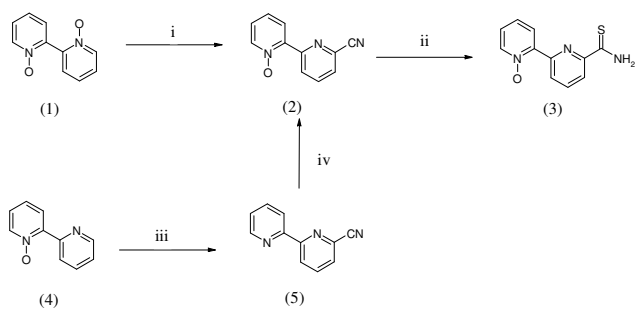
and washed with EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) and dried *in vacuo* to give L<sup>7</sup>•HBr. The hydrobromide salt was then suspended in aqueous ammonia (0.88 sp.gr., 5 ml) for 12 hours, filtered and washed with water (2 x 2 ml), EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) giving L<sup>7</sup> as a pale yellow solid (0.11 g, 52 %). <sup>1</sup>H NMR (500 MHz, d<sup>6</sup>-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<sup>+</sup>). Found: C, 66.4; H, 3.6; N, 13.9%; C<sub>27</sub>H<sub>17</sub>N<sub>5</sub>OS<sub>2</sub> requires C, 66.0; H, 3.5; N, 14.2%.

**Synthesis of L<sup>8</sup>.** 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 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) and dried *in vacuo* to give L<sup>8</sup>•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 x 2 ml), EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) giving L<sup>8</sup> as a pale yellow solid (0.065 g, 49 %). As with L<sup>6</sup> the solubility of the ligand was very poor, even in d<sup>6</sup>-DMSO at 80 °C and precluded <sup>1</sup>H NMR analysis. ESI-MS *m/z* 616 (M + H<sup>+</sup>). Found: C, 64.8; H, 3.9; N, 13.2%; C<sub>33</sub>H<sub>22</sub>N<sub>6</sub>O<sub>3</sub>S<sub>2</sub> 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<sup>5</sup>) or MeNO<sub>2</sub> (L<sup>6</sup> – L<sup>8</sup>) and the reaction heated and sonicated until complete dissolution. Slow diffusion of dichloromethane ([Cu<sub>2</sub>(L<sup>7</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> and [Co<sub>4</sub>(L<sup>8</sup>)<sub>4</sub>](BF<sub>4</sub>)<sub>8</sub>), diethyl ether (Cu(L<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>) and ethyl acetate ([Ni<sub>2</sub>(L<sup>6</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>) gave crystalline materials which were isolated by filtration, washed with the diffusion solvent and dried under vacuum. [Cu(L<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(MeCN)][Cu(L<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)] (yield = 43 %) Found: C, 36.4; H, 2.6; N, 9.8%. Calculated for C<sub>38</sub>H<sub>29</sub>N<sub>9</sub>O<sub>19</sub>S<sub>2</sub>Cu<sub>2</sub>Cl<sub>4</sub>: C, 36.6; H, 2.3; N, 10.1%. [Ni<sub>2</sub>(L<sup>6</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (yield = 65 %) Found: C, 40.4; H, 1.8; N, 10.8%. Calculated for C<sub>52</sub>H<sub>32</sub>N<sub>12</sub>O<sub>20</sub>S<sub>4</sub>Ni<sub>2</sub>Cl<sub>4</sub>: C, 40.8; H, 2.1; N, 11.0%. [Cu<sub>2</sub>(L<sup>7</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (yield = 53 %) Found: C, 42.8; H, 2.4; N, 9.1%. Calculated for C<sub>54</sub>H<sub>34</sub>N<sub>10</sub>O<sub>18</sub>S<sub>4</sub>Cu<sub>2</sub>Cl<sub>4</sub>: C, 43.0; H, 2.3; N, 9.3%. [Co<sub>4</sub>(L<sup>8</sup>)<sub>4</sub>](BF<sub>4</sub>)<sub>8</sub> (yield = 47 %) Found: C, 44.8; H, 2.2; N, 9.1%. Calculated for C<sub>132</sub>H<sub>88</sub>N<sub>24</sub>O<sub>12</sub>S<sub>8</sub>Co<sub>4</sub>B<sub>8</sub>F<sub>32</sub>C<sub>2</sub>H<sub>4</sub>Cl<sub>4</sub>: C, 45.2; H, 2.6; N, 9.5%.

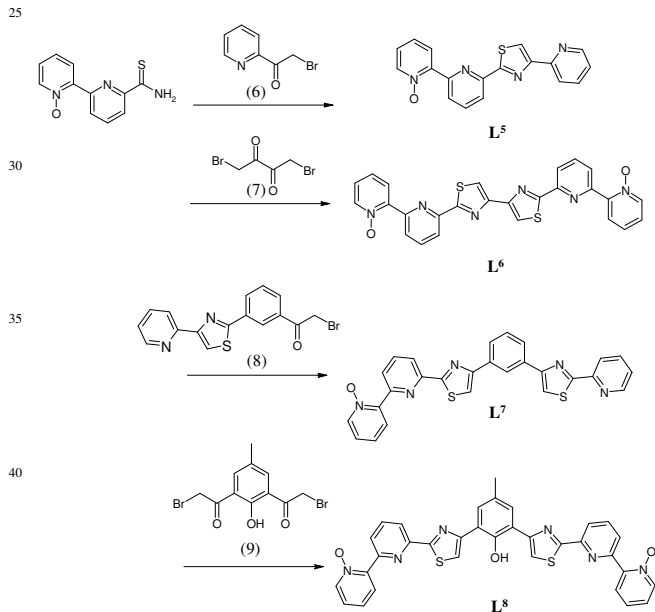
## Results and Discussion

### Ligand Synthesis



**Scheme 1** Synthesis of 6'-cyano-2,2'-bipyridine-1-oxide. Reagents and conditions i) TMSCN, BzCl, CH<sub>2</sub>Cl<sub>2</sub>, reflux; ii) H<sub>2</sub>S, Et<sub>3</sub>N, EtOH, RT; iii) TMSCN, BzCl, CH<sub>2</sub>Cl<sub>2</sub>, reflux; iv) mCPBA, CH<sub>2</sub>Cl<sub>2</sub>, RT;

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 mCPBA 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  $\alpha$ -bromoacetyls (**6**) – (**9**) either in EtOH or DMF followed by deprotonation with concentrated ammonia gave the corresponding ligands **L**<sup>5</sup> – **L**<sup>8</sup> (Scheme 2).



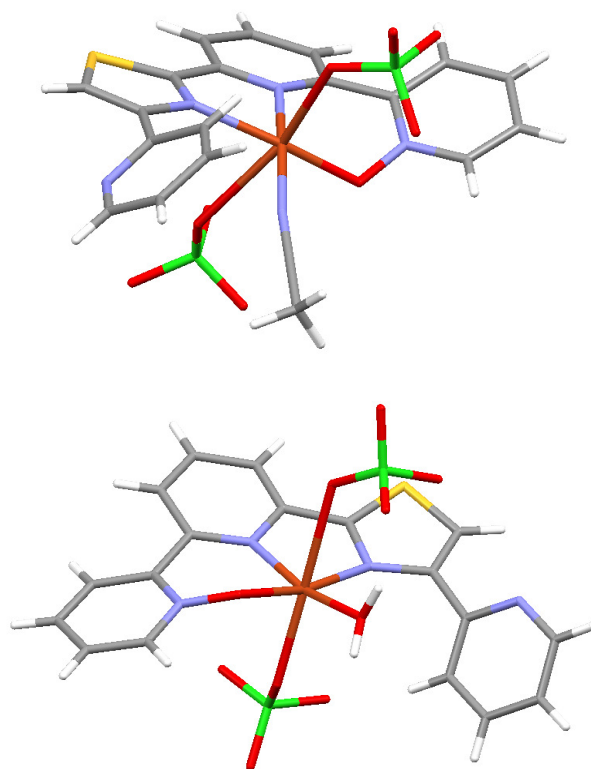
**Scheme 2** Synthesis of ligands **L**<sup>5</sup> – **L**<sup>8</sup>.

## Coordination Chemistry

Reaction of ligand **L**<sup>5</sup> with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

Reaction of **L**<sup>5</sup> with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeCN gave a green solution from which crystals were obtained by slow diffusion of ethyl acetate. 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**<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(sol)] where sol = H<sub>2</sub>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.

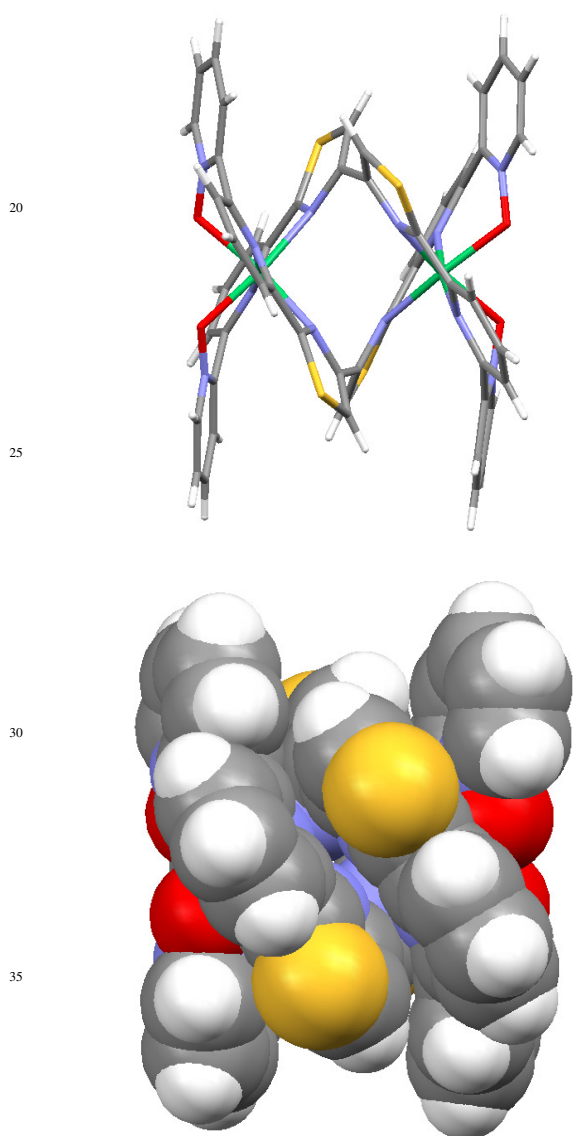
In the ESI-MS an ion is observed at  $m/z = 494$  which corresponds to {[Cu(**L**<sup>5</sup>)]ClO<sub>4</sub>}<sup>+</sup>, however higher molecular weight ions at  $m/z = 1088, 1683, 2280$  and  $2873$  which correspond to {[Cu<sub>n</sub>(**L**<sup>5</sup>)<sub>n</sub>](ClO<sub>4</sub>)<sub>2n-1</sub>}<sup>+</sup>, 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.



**Fig. 2** X-ray crystal structure of [Cu(**L**<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(MeCN)] (top) and [Cu(**L**<sup>5</sup>)(ClO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)] (bottom).

Reaction of ligand  $L^6$  with  $Ni(ClO_4)_2 \cdot 6H_2O$ .

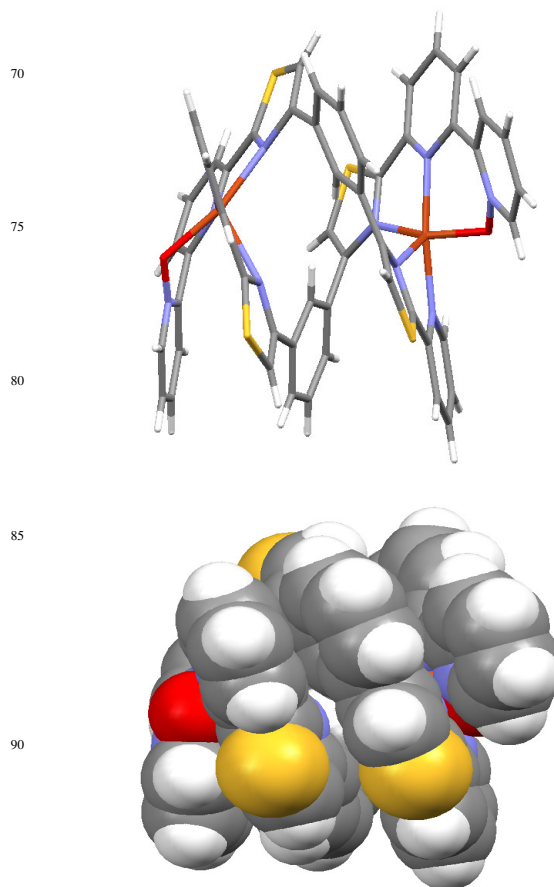
Reaction of ligand  $L^6$  with  $Ni(ClO_4)_2 \cdot 6H_2O$  in  $MeNO_2$  gives a green solution from which light green crystals are produced after slow diffusion of tetrahydrofuran. ESI-MS analysis gave a remarkably simple spectrum with ions at  $m/z = 1433, 922$  and  $665$  corresponding to  $\{[Ni_2(L^6)_2](ClO_4)_3\}^+$ ,  $\{[Ni_2(L^6)](ClO_4)_3\}^+$  and  $\{[Ni_2(L^6)_2](ClO_4)_2\}^{2+}$ . Solid-state analysis shows the formation of a dinuclear double helicate  $[Ni_2(L^6)_2]^{4+}$ ; 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).



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

Reaction of ligand  $L^7$  with  $Cu(ClO_4)_2 \cdot 6H_2O$ .

Reaction of ligand  $L^7$  with  $Cu(ClO_4)_2 \cdot 6H_2O$  in  $MeNO_2$  gives a green solution from which green crystals were produced upon slow diffusion of  $CH_2Cl_2$ . As with the  $Ni^{2+}$  complex, the ESI-MS analysis was straightforward with ions at  $m/z = 1407$  and  $915$  corresponding to  $\{[Cu_2(L^7)_2](ClO_4)_3\}^+$  and  $\{[Cu_2(L^7)](ClO_4)_3\}^+$ . Solid-state analysis shows the formation of a head-to-tail dinuclear double helicate  $[Cu_2(L^7)_2]^{4+}$  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 helicites 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 (c.f.  $[Cd_2(L^1)_2]^{4+}$  inter-ligand phenyl separation  $4.2$  Å).

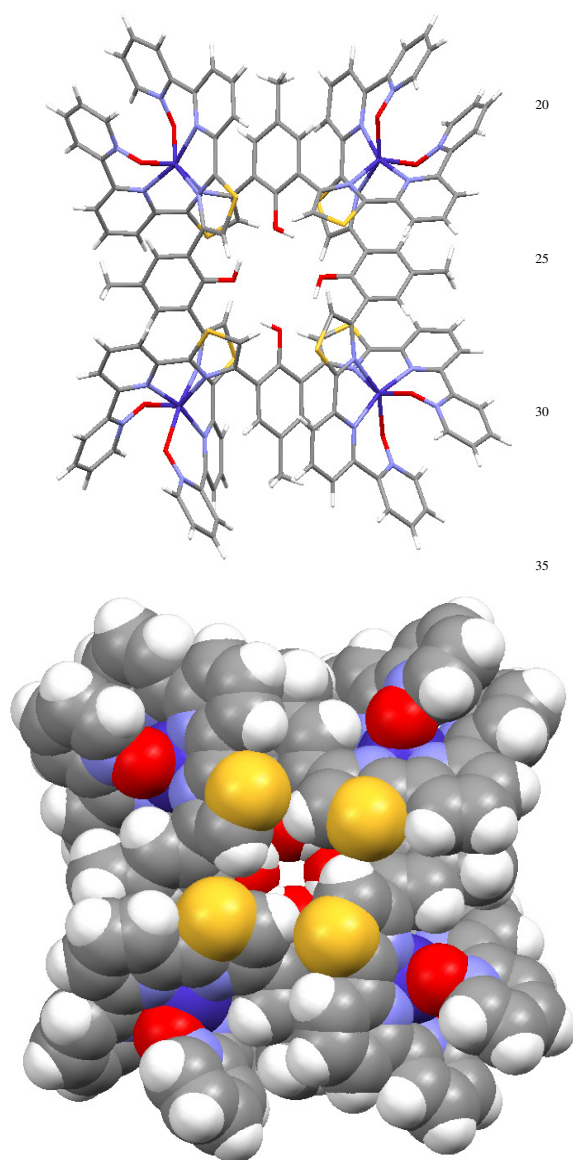


**Fig. 4** X-ray crystal structure of  $[Cu_2(L^7)_2]^{4+}$  (top) and as a space-filling model (bottom).



Reaction of ligand  $L^8$  with  $Co(BF_4)_2 \cdot 6H_2O$ .

Ligand  $L^8$  contains two thiazole-pyridyl-pyridyl-N-oxide donor units separated by a 1,3-phenol spacer. Upon reaction of this ligand with  $Co(BF_4)_2 \cdot 6H_2O$  a pale orange solution results from which crystals were produced upon slow diffusion of dichloromethane. Solid state analysis shows the formation of a tetranuclear cyclic helicate  $[Co_4(L^8)_4]^{8+}$ , 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.



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

40 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 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  $[Co_4(L^8)_4]^{8+}$  ( $\sim 8.0$  Å) than the pentanuclear species  $[Zn_5(L^1)_5]^{10+}$  ( $\sim 7.0$  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.<sup>8</sup> 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.

#### Acknowledgements

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#### 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 1<sup>st</sup> row transition metal ions.<sup>3,6,8,11</sup> 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.

#### Notes and references

<sup>a a</sup> Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield, HD1 3DH. Fax: +44 (0) 148-447-2182; Tel: +44 (0) 148-447-3759; E-mail: c.r.rice@hud.ac.uk.

<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

<sup>‡</sup> Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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