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

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

A series of ligands that contain both N-donor and N-oxide donor atoms have been synthesised and ligands L⁵, L⁶, L⁷ and L⁸ contain, 4, 6, 5, and 6 donor atoms respectively. The smallest ligand L⁵ forms a mononuclear complex with Cu²⁺ ([Cu(L⁵)(ClO₄)₂(MeCN)]) whereas L⁶ and L⁷ form dinuclear double helicates with Ni²⁺ and Cu²⁺ respectively ([Ni₂(L⁶)₂]⁴⁺ and [Cu₂(L⁷)₂]⁴⁺). L⁸ forms a tetranuclear cyclic helicate upon reaction with Co²⁺ ([Co₄(L⁸)₄]⁸⁺) and in all cases the complexes are characterised by single-crystal X-ray diffraction and ESI-MS. The N-oxide units impart 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 dependent upon the ionic radius of the metal ion used to coordinate the ligand strand. Reaction of L¹ with Cd²⁺ ions gives a relatively simple dinuclear double helicate [Cd₂(L¹)₂]⁴⁺ whilst Zn²⁺ ions result in the assembly of a pentanuclear cyclic helicate [Zn₅(L¹)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 (L¹ and

![Fig. 1 Ligands L¹–L⁴](image-url)
L$^+$) and this partitions the ligand into two separate binding domains with the N-oxide bridging the metal ion. Specifically, reaction of L$^+$ with Cd$^{2+}$ gives a dinuclear double helicate with each of the Cd$^{2+}$ ions coordinated by the N-oxide and pyridyl thiazole donor of two different ligands giving the complex [Cd$_2$(L$^+$)$_2$]$^{4+}$.$^9$ 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(Kα) 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$_2$(L$^+$)$_2$]$^{8+}$ 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$^+$)$_2$][ClO$_4$]$_2$.[MeCN][Cu(L$^+$)][ClO$_4$](H$_2$O)]: M = 1447.60, Triclinic, PI, a = 9.4086(8), b = 16.9828(14), c = 18.2559(16), $\alpha$ = 67.070(2), $\beta$ = 82.993(2), $\gamma$ = 74.439(2)$^o$, $V$ = 2587.54(4) Å$^3$, Z = 2; $\rho$calc = 1.858 Mg m$^{-3}$, F(000) = 1456; dimensions 0.35 × 0.3 × 0.1 mm$^3$; $\mu$(MoKα) = 1.314 mm$^{-1}$, $T$ = 100 K. A total of 15 306 reflections were measured in the range 1.21 $\leq$ θ $\leq$ 26.02$^o$ (hkI range indices: $-$11 $\leq$ h $\leq$ 7, $-$20 $\leq$ k $\leq$ 20, $-$21 $\leq$ l $\leq$ 22), 10 037 unique reflections ($R_{int}$ = 0.0645). The structure was refined on $F^2$ to $R_{wp}$ = 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 [Ni$_2$(L$^+$)$_2$][ClO$_4$]$_2$.[MeNO$_2$]$_5$(H$_2$O)$_2$]: M = 3384.92, Triclinic, PI, $a$ = 17.9775(15), $b$ = 21.8353(18), $c$ = 24.415(2) Å, $\alpha$ = 105.485(2), $\beta$ = 95.760(2), $\gamma$ = 103.275(2)$^o$, $V$ = 8862.21(13) Å$^3$, Z = 2; $\rho$calc = 1.620 Mg m$^{-3}$, F(000) = 4351; dimensions 0.31 × 0.1 × 0.1 mm$^3$; $\mu$(MoKα) = 0.854 mm$^{-1}$, $T$ = 150(2) K. A total of 164 320 reflections were measured in the range 1.52 $\leq$ θ $\leq$ 27.50$^o$ (hkI range indices: $-$23 $\leq$ h $\leq$ 23, $-$26 $\leq$ k $\leq$ 28, $-$28 $\leq$ l $\leq$ 31), 39 488 unique reflections ($R_{int}$ = 0.0802). The structure was refined on $F^2$ to $R_{wp}$ = 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. $^1$H NMR spectra were recorded on a 400 MHz Bruker Avance DXP400. Mass spectra were obtained on a Bruker MicroTOF-q LC mass spectrometer. Extreme care should be taken when using TMS CN 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, 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) gave (2) as a sandy solid (0.12 g, 0.61 mmol, 57%). $^1$H NMR (500 MHz, CDCl$_3$) 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),
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%).

Synthesis of 1-N-oxide-2,2′-bipyridine-6′-thioamide. To a solution of the cyano compound (2) (0.07 g, 3.55 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol, 1.38 ml) was added and H2S 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 (1) as a yellow solid (0.081 g, 0.24 mmol, 57%). 1H NMR (400 MHz, CDCl3) δ (ppm) 8.86 (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).

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 C11H7N3NaO3 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%).

Synthesis of 1-N-oxide-2,2′-bipyridine-6′-thioamide. To a solution of the cyano compound (2) (0.07 g, 3.55 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol, 1.38 ml) was added and H2S was slowly bubbled through the solution for 15 minutes, during which time the solution turned yellow. The yellow solution was allowed to stand for 46 hours during which time a yellow solid slowly precipitated. Collection via filtration gave pure (1) as a yellow solid (0.081 g, 0.24 mmol, 57%). 1H NMR (400 MHz, CDCl3) δ (ppm) 8.86 (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).

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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 tetramethylsilylecyanide 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 thioamid (3) with α-bromoacetyl (6)–(9) either in EtOH or DMF followed by deprotonation with concentrated ammonia gave the corresponding ligands L5–L8 (Scheme 2).

Coordination chemistry

Reaction of ligand L5 with Cu(ClO4)2·6H2O. Reaction of L5 with Cu(ClO4)2·6H2O 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, CH2Cl2, reflux; (ii) H2S, Et3N, EtOH, RT; (iii) TMSCN, BzCl, CH2Cl2, reflux; (iv) mCPBA, CH2Cl2, RT.

Scheme 2  Synthesis of ligands L5–L8.

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(L5)·(ClO4)2(sol)] where sol = H2O or MeCN (Fig. 2) [Cu–N:
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Solid state analysis shows the formation of a tetranuclear cyclic helicate \([\text{Co}_4(L^8)_4]^{3+}\), where each of the ligands has separated into tridentate thiazole-pyrlydyl-pyrlydyl-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
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 centroids of the central pyridine rings in adjacent ligand strands show that the distance is substantially longer in [Co₄(L₈)₄]⁸⁺ (~8.0 Å) than the pentanuclear species [Zn₅(L₁)₅]¹⁰⁺ (~7.0 Å). ESI-MS shows a doubly charged ion at m/z = 1607 corresponding to the tetranuclear cyclic helicate ([Co₄(L₈)₄][ClO₄]⁶)²⁺. Also an ion at m/z = 2454 corresponding to ([Co₃(L₈)₃][ClO₄]₂)⁺ 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 L⁷ 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 L⁶ with other metals such as Co²⁺, Fe²⁺, or Zn²⁺ would all give the dinuclear double helicate species [M₂(L₆)₂]⁺ however despite attempts we cannot obtain crystals of sufficient quality to confirm this.
Acknowledgements

This work was supported by the University of Huddersfield.

Notes and references


