Introduction

The construction of metal organic coordination networks has developed rapidly over recent years, with the appearance of many rationally designed networks prepared using the concepts of crystal engineering.1,2 Interest in these compounds has been motivated not only due to their interesting structures, but as a method to obtain solid materials with diverse applications in catalysis,3 gas storage, magnetism,4 and luminescence.5 As a result, a variety of networks with interesting structures and topologies have been reported, and in particular, rigid organic ligands based upon N-donor ligands such as 4,4′-bipyridine (4,4′-bpy) have been heavily utilised, since they afford a high degree of control over the resulting coordination frameworks. Similarly, due to their more predictable coordination geometry, a large majority of research efforts in this area have focused on the use of d-block transition metal cations or clusters.

Nonetheless, it remains a challenge for polymeric structures with higher topological connectivity to be generated with d-block metal ions due to their limited coordination numbers, and even six-connected nodes are uncommon when using heterocyclic N-donor ligands. The use of trivalent lanthanide cations as metal centered nodes with their larger ionic radii and much higher coordination numbers is attractive, since these 4f-block metal ions can allow for new and unusual network topologies to be prepared. Similarly, the unique electronic structures of the Ln(III) cations can furnish complexes which have highly specific and sought after magnetic and optical properties.

A variety of Ln(iii) organic frameworks have been prepared using O-donor ligands such as 1,4-benzenedicarboxylate, which have been shown to demonstrate interesting sorption and luminescence properties.6–8 By contrast, only a limited number of Ln(III) coordination polymers with N-donor ligands such as 4,4′-bpy have been reported,9,10 due to the much lower affinity of these ligands for the oxophilic Ln(III) metal centers. However, facile oxidation of the nitrogen atoms provide N-oxide derivatives,11 which are far more suitable donors, and in early 2000, Schröder and Champness reported12 the first Ln(III)
coordination networks based on 4,4′-bipyridine-N,N′-dioxide (4,4′-bpdo, Chart 1). Shortly thereafter, the same authors prepared and structurally characterised an unprecedented eight connected lanthanide coordination network with the CsCl (4′-4δ) network topology, with recent work extending the chemistry of substituted 4,4′-bpdo ligands.

Interestingly then, although the isomeric 3,3′-bipyridine-N,N′-dioxide (3,3′-bpdo, Chart 1) compound is known in the literature, it appears that its coordination properties with metal ions have never been explored. Due to free rotation of the N-oxides) when acting as a bidentate ligand, and rationalised this may introduce additional structural diversity into its networks. Herein, we report the synthesis and structural characterisation of two novel coordination polymers derived from 3,3′-bpdo and Yb(m), and compare these to similar networks obtained using 4,4′-bpdo under identical conditions, in the presence of ‘coordinating’ (NO₃⁻) or ‘non-coordinating’ (CF₃SO₃⁻) anions.

**Experimental**

**General**

All starting reagents were purchased from commercial suppliers (Sigma Aldrich, Alpha Aesar) and were used without further purification. Solvents were dried over activated 3 Å molecular sieves prior to use. 4,4′-bipyridine is commercially available, while the corresponding 3,3′-bipyridine is commercially unavailable, while the corresponding 3,3′-bpdo was isolated as a pale yellow powder (2.46 g, 90%) that gave analytical data consistent with those previously reported. 3,3′-bpdo was isolated as a white powder (3.95 g, 94.8%) ¹H NMR (δ: J = 7.68 (ddd, 2H, J = 8.0, 6.4, 0.4 Hz), 7.93 (ddd, J = 8.0, 1.7, 1.0 Hz), 8.43 (ddd, J = 6.4, 1.7, 1.0 Hz), 8.75 (dt, 2H, J = 1.7, 0.6 Hz), LR-ESI-MS: (m/z) 189.07. Anal. Calcd [Found] for C₁₁H₁₁N₅O₁₂Yb (189.99 g mol⁻¹): C, 63.83 (63.30); H, 4.29 (4.25); N, 14.89 (14.41).

**Metal complexes.** Synthesis of metal complexes and crystallisations were undertaken using diffusion solvent mixture techniques. Approx. 20 mg of solid Ln(m) metal salts (Yb₅ₓ·xH₂O, where X = NO₃⁻ or CF₃SO₃⁻, x = 5) were placed at the bottom of a glass vial and were covered with a chlorinated anti solvent (CHCl₃, ca. 10 mL) over which a solution of the respective bipyridyl-N,N′-dioxide (20 mg) dissolved in MeOH (ca. 10 mL) was carefully layered. Over a period of ca. 2–3 weeks, the solid metal salts gradually dissolved in the solvent mixture and subsequent formation of crystalline products at the solvent interface on the wall of the vial was observed. Single crystals suitable for structural analysis were selected and analysed by X-ray diffraction.

**Synthesis**

**Organic ligands.** The required 4,4′- and 3,3′-bipyridyl-N,N′-dioxide ligands were prepared using a modified literature procedure. Briefly, the appropriate 4,4′- or 3,3′-bipyridine (1 equiv.) was dissolved in a small volume of glacial acetic acid and 30% hydrogen peroxide (3 equiv.) was added dropwise with heating at 70–80 °C over a 3 h period. An additional 1 equiv. of 30% hydrogen peroxide was added and the temperature maintained at 70–80 °C overnight. Upon cooling, acetone was added to give a crude precipitate which was recrystallized from hot water by the addition of a large excess of acetone, vacuum filtered and air dried. 4,4′-bpdo was isolated as a pale yellow powder (2.46 g, 90%) that gave analytical data consistent with those previously reported. 3,3′-bpdo was isolated as a white powder (3.95 g, 94.8%) ¹H NMR (δ: J = 7.68 (ddd, 2H, J = 8.0, 6.4, 0.4 Hz), 7.93 (ddd, J = 8.0, 1.7, 1.0 Hz), 8.43 (ddd, J = 6.4, 1.7, 1.0 Hz), 8.75 (dt, 2H, J = 1.7, 0.6 Hz), LR-ESI-MS: (m/z) 189.07. Anal. Calcd [Found] for C₁₁H₁₁N₅O₁₂Yb (189.99 g mol⁻¹): C, 63.83 (63.30); H, 4.29 (4.25); N, 14.89 (14.41).
residual d$_2$-MeOD solvent peak ($\delta = 3.34$ ppm).\(^1\) Low Resolution Electro-Spray Ionisation Mass Spectrometry (LR-ESI-MS) was carried out using a Bruker ESI-QTOF instrument with Bruker ESI source. Elemental analyses were undertaken by the Analytical Services Unit of the School of Chemistry and Molecular Biosciences, University of Queensland. Emission and excitation spectra were acquired using a Horiba JY FluoroLog-3 spectrofluorimeter equipped with liquid N$_2$ cooled DSS-IGA020L InGaAs detector. Spectra were reference corrected for the excitation light source variation (lamp and grating).

**X-ray crystallography**

Data were with collected using an Oxford Diffraction Gemini CCD diffractometer, employing confocal mirror monochromated Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) or graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) with $\omega$ and $\psi$ scans at 190 K. Data integration, reduction and absorption corrections were performed using the CrysAlisPro software package.\(^2\) Structures were solved by direct methods using SIR97\(^2\) and refined by full-matrix least-squares analysis with SHELXL-2014\(^2\) using WinGX-32.\(^2\) All non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. H atoms bonded to O or N atoms were located in the difference Fourier map before refinement, while C bound H atoms were included in idealised positions and refined using a riding model. Disorder was modelled using standard crystallographic methods with further details given in the ESI.\(^†\) In particular for (3), several anions and solvent molecules were disordered, with only four CF$_3$SO$_3^-$ anions being located, which were modelled over eight positions. The remaining anion and solvent molecules were smeared over a large volume. Accordingly, this contribution to the electron density was treated using the SQUEEZE\(^2\)\(^4\) routing in PLATON\(^2\)\(^5\) resulting in satisfactory residuals. Despite these problems, the connectivity of the structure is unambiguous. Molecular drawings were produced with Mercury 3.3.\(^2\)\(^6\)

**Computational studies**

Ground state density functional theory (DFT) calculations were performed with Gaussian03,\(^2\)\(^7\) using the B3LYP/6-31G$^\text{\small +}\$ basis set and input coordinates derived from MM2 minimised molecular models. All calculations were done in the gas phase and geometry optimisations were performed with no symmetry restraints. The dihedral angle of the aromatic C-C linkage between N-oxide groups was constrained to be either 0° or 180°.

**Results and discussion**

The required 3,3′- and 4,4′-bipyridine-N,N′-dioxide ligands were readily prepared in high yield using well-known peracid oxidation techniques (CH$_3$COOH/H$_2$O$_2$), and a variety of novel coordination polymers have been obtained herein upon reaction with YbX$_3$ salts ($X = NO$_3^-$, CF$_3$SO$_3^-$). For the purpose of the present study, we have focused on the preparation and characterisation of X-ray quality crystals with identical (or very similar) coordination spheres about the metal cation, in order to facilitate a comparison of the coordinating properties of the 4,4′-bdpo vs. 3,3′-bdpo ligands. However, we recognise that other structure types may also be possible, which has been demonstrated previously\(^1\)\(^8\) for the reaction of Tb(NO$_3$)$_3$·$x$H$_2$O with 4,4′-bdpo, which forms a variety of networks differing in the final M:L stoichiometry or solvation of the metal cation.

$$\left[\text{Yb}(4,4′\text{-bdpo})(\text{NO}_3)_3(\text{CH}_3\text{OH})\right]_\infty \text{ (1)}$$

The structure of (1) (Fig. 1) is comprised of a 1D coordination polymer built from repeating zig-zag chains of linked Yb(m) cations. Each of the metal centres are nine-coordinate (CN = 9), with the YbO$_5$ coordination sphere provided by one oxygen atom from each of two different bridging bidentate 4,4′-bdpo ligands, one O atom from a coordinated solvent methanol, and six other O atoms from three bidentate coordinated nitrate anions. The metal cation lies on the crystallographic twofold axis, with two 4,4′-bdpo ligands (which are essentially planar) occupying adjacent coordination sites and forming a ‘V-joint’ at the metal centres, causing the zig-zag chain to undulate with a Yb–Yb separation in the crystal is ca. 101°. Two of the coordinated NO$_3^-$ anions, similarly related by the crystallographic twofold axis, sit adjacent to the 4,4′-bdpo ligands while the third, which lies in a more apical position, is disordered equally over two sites, with the other disordered component identified as a coordinated CH$_3$OH solvent molecule.

Neighbouring Yb(m) centres of the 1D coordination polymer chain are separated at a distance of ca. 13.1 Å, while the shortest interchain Yb···Yb separation in the crystal is ca. 8.2 Å. Interestingly, an intermolecular hydrogen bonding interaction is also evident between the O atom of the coordinated methanol and the nitrate anion on an adjacent chain (O1M1···O32 = 2.718 Å). Overall, the obtained structure is isostructural with a previously reported\(^1\)\(^8\) complex of Tb(m) with 4,4′-bdpo, where a similar zig-zag chain was obtained with a 1:2 stoichiometry. In the present case, the smaller ionic radius\(^2\)\(^8\) of Yb(m) (1.042 Å cf. 1.095 Å) leads to a slight decrease in the coordinate bond lengths (2.20 Å cf. 2.27 Å) and small changes to the bond angles, but the overall structural topology remains unchanged.
\{[\text{Yb}(3,3\text{-bpdo})\text{]}\text{](NO}_3\text{)}\text{]}_2(\text{CH}_3\text{OH}_2(\text{CHCl}_3))\text{]}_\infty (2)

The structure of (2) is also comprised of a zig-zag chain (Fig. 1) which forms an extended 1D coordination polymer, and reveals an identical YbO$_6$ coordination environment about the central metal cation. The nine O donor atoms are provided by three bidentate NO$_3^-$ anions, a bridging bidentate 3,3-bpdo ligand and the O atom of a disordered coordinated CH$_3$OH solvent molecule. By analogy to the structure of (1), the 3,3-bpdo ligands similarly occupy adjacent coordination sites on the Yb(u) metal centre, with two adjacent NO$_3^-$ anions located in equatorial positions, and a single NO$_3^-$ anion and coordinated CH$_3$OH solvent molecule occupying more apical positions with respect to the N-oxide ligands.

However, unlike the structure of (1), the zig-zag chain structure of (2) is much more condensed due to the very different bond vector presented by the bridging bidentate 3,3'-bpdo ligands, which have adopted a ‘cisoid’ arrangement of their N-oxide donor groups (i.e. 60° instead of 180°). This causes the coordination polymer chain to undulate with a much more acute Yb---Yb bond angle of ca. 50°, resulting in an intrachain separation between adjacent Yb(u) centres of ca. 9.2 Å, but a much shorter interchain separation of ca. 6.3 Å between metal cations. We also note that the aromatic rings of the coordinated 3,3'-bpdo ligand are not planar, but are instead offset by rotation about the central C=C bond, with an apparent torsion angle of ca. 47°. This arrangement allows one of the aromatic rings to form an offset face-to-face π-π stacking arrangement, interdigitated with adjacent 1D polymer chains.

\{[\text{Yb}(4,4\text{-bpdo})\text{]}\text{][CF}_3\text{SO}_3\text{]}_2(\text{CH}_3\text{OH}_2(\text{CHCl}_3))\text{]}_\infty (3)

The structure we obtain upon reaction of Yb(CF$_3$SO$_3$)$_2$·xH$_2$O with 4,4'-bpdo is identical to that reported$^{29}$ by Schröder and Champness, however we include a brief description here for comparison. A complex binodal 3D network is apparent, with each Yb(u) metal ion being eight coordinate (CN = 8). There are three independent Yb(u) centres in the asymmetric unit, with the nearest adjacent Yb---Yb bondlengths being similar, but non-equivalent at Yb1---Yb2 = 13.03 Å, Yb1---Yb3 = 13.03 Å and Yb2---Yb3 = 13.13 Å. The YbO$_6$ donor set is provided by four bridging bidentate 4,4'-bpdo ligands, that form layers of perpendicularly linked (6,3) nets, which are intersected by an additional two (4,4) nets to form a complicated (3$^2$,4$^2$,5$^2$)$^\top$ network topology. The remaining voids within the network are occupied by the CF$_3$SO$_3^-$ anions, which were disordered, and not all of which could be located from the difference map, both in the previously reported data and our results presented herein. A view of the structure is shown in Fig. 2.

\{[\text{Yb}(3,3\text{-bpdo})\text{]}\text{][CF}_3\text{SO}_3\text{]}_2(\text{CH}_3\text{OH}_2(\text{CHCl}_3))\text{]}_\infty (4)

The X-ray structure of (4) is shown in Fig. 3. Each of the Yb(u) centres are seven coordinate (CN = 7) with the YbO$_7$ donor set provided by three bridging bidentate 3,3'-bpdo ligands and the unexpected monodentate coordination of a CF$_3$SO$_3^-$ anion. The CF$_3$SO$_3^-$ anion is typically considered to be non-coordinating,$^{30}$ although there are several examples where metal complexation has been structurally characterised, typically in combination with larger charge neutral ligands$^{31}$ or in ionic liquids.$^{32}$ This reduces the overall connectivity of the metal node from eight, observed in the structure of (3), to six in the present case, with a concomitant decrease in the coordination number of the metal ion from CN = 8 to CN = 7 likely as a result of steric requirements from the inner sphere anion.

Considering each of the 3,3'-bpdo ligands as a unique link, an overall 2$^2$,4$^2$,6$^2$ network topology which forms an extended 2D sheet is observed. There are two types of connections evident in this network between six connecting nodes. In the first case, two pairs of bridging cis N-oxide 3,3'-bdpo ligands form short linkages between adjacent Yb(u) metal centres, with Yb---Yb separations of 8.1 Å and 10.1 Å. By contrast, the remaining two bridging bidentate 3,3-bpdo ligands which form single links between each metal are coordinated with N-oxide donors in a trans orientation, leading to a longer Yb---Yb separation of 11.2 Å. Importantly, if the aforementioned double links are considered as a single link, the topological description is reduced to the more simple Wells (4,4) net.
(i.e. 4\textsuperscript{1}-6\textsuperscript{2} topology), with \textit{trans} N-oxides interconnecting double bridged Yb(\textit{iii}) centres that form 1D chains running along the crystallographic \textit{c}-axis. Remaining within the asymmetric unit are three co-crystallised CHCl\textsubscript{3} molecules, a disordered CH\textsubscript{3}OH solvent and the other two CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} anions (one of which is disordered) all located between the adjacent 2D sheets.

Density functional theory (DFT) calculations

In an effort to rationalise the observed differences in coordination behaviour comparing the 4,4′-bpdo and 3,3′-bpdo ligands, we have also undertaken static DFT calculations at the B3LYP/6-31G\textsuperscript{*} level of theory to understand any differences in the charge distribution of the aromatic N-oxide groups. Initially, we suspected that a difference in the polarisation of the N=O bond for the two differing isomers (leading to a more electropositive Yb(\textit{iii}) centre for complexes with 3,3′-bdpo) may result in a higher tendency for inner sphere coordination of the CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} anion. However, as shown in Fig. 4, the resulting Electro-Static Potential (ESP) maps do not show any significant differences in the polarity of the N=O bond. Since the difference in coordination tendency cannot be attributed to electrostatics, we attribute the difference observed in coordination behaviour to the different steric requirements of the 3,3′-bdpo and 4,4′-bdpo ligands.

Emission and excitation spectroscopy

Given their significantly different X-ray structures, we were also interested in the luminescence behaviour of the coordination polymers obtained using CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} as the anion. Hence, emission spectra obtained for solid samples of (3) and (4) upon excitation in the UV region are shown in Fig. 5. The well-known emission spectrum of the Yb(\textit{iii}) cation in the Near Infra-Red (NIR) region, due to the slightly different electronic structure of the organic 4,4′-bdpo and 3,3′-bdpo ligands, which act as light harvesting antennae for the observed NIR emission. Upon dissolving solid samples of (3) and (4) in MeOH, the NIR emission of the Yb(\textit{iii}) cation was no longer observed upon UV excitation, and the UV-Vis spectra of the resulting solutions instead appear very similar to the spectra of the free 3,3′-bdpo and 4,4′-bdpo ligands (see Fig. S1\textsuperscript{†}), suggesting the coordination polymer structure is not retained in solution, likely as a result of competing solvent coordination.

Conclusions

A series of coordination polymers utilising Yb(\textit{iii}) and the isomeric 3,3′-bdpo and 4,4′-bdpo ligands have been prepared and structurally characterised using X-ray techniques. As anticipated, the 3,3′-bdpo ligand acts as a highly versatile linker, due to the possibility of both \textit{cis} or \textit{trans} orientations for the N-oxide donor groups, and the presence of both conformers has been identified in the resulting 2D sheet using CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} as a counter ion. The unexpected inner sphere coordination of the CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} anion ultimately decreased the connectivity of the metal centered node, which as a result of the differing local symmetry of the metal centre, leads to a considerable different lineshape for the sensitised NIR emission band from the Yb(\textit{iii}) cation. We are currently exploring the coordination behaviour of 3,3′-bdpo as a novel ligand for other Ln(\textit{iii}) cations with a variety of differing anions.

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Notes and references