FULL PAPER

Constructing Terbium Co-ordination Polymers of 4,4′-Bipyridine-*N*,*N*′-dioxide by Means of Diffusion Solvent Mixtures

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Abstract: Five different co-ordination polymers of terbium(III) and the bidentate ligand 4,4′-bipyridine-*N*,*N*′-dioxide (L), $[Tb(L)(CH_3OH)(NO_3)_3]_\infty$ (**1**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot CH_2Cl_2\}_\infty$ (**2**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot CH_3OH \cdot 0.8H_2O\}_\infty$ (**3**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot 0.4C_2Cl_4 \cdot 0.8CH_3OH\}_\infty$ (**4**), and $[Tb(L)_2(NO_3)_3]_\infty$ (**5**) have been synthesised by the use of different "diffusion solvent mixtures", and structurally characterised by X-ray crystallography. Compound **1**, with a Tb:L stoichiometry of 1:1, adopts a zig-zag chain structure, which forms three-fold interpenetrating diamondoid frameworks through interchain hydrogen bonding between co-ordinated methanol and a nitrate group on an adjacent chain. Polymers **2**, **3**, and **4** all have a Tb:L stoichiometry of 1:1.5, but adopt different topologies. For **2**, a ladder arrangement is found and large channels which accommodate solvent CH_2Cl_2 molecules are formed by superposition of the ladders. For **3** and **4** 4.8^2 net structures are observed. The superposition of the 4.8^2 nets in **3** and **4**, by disposing adjacent layers such that every octagon is positioned below a tetragon from the neighbouring layer, allows the formation of two kinds of channel, with that inside the tetragons accommodating methanol molecules. The other kind of channel, between tetragons, accommodates water molecules in the case of **3** and tetrachloroethylene molecules in the case of **4**. Compound **5**, with a Tb:L stoichiometry of 1:2, has a linear polymeric structure with one bridging and one terminal ligand, and forms (6,3) plane nets by means of intermolecular electrostatic interactions between *N*-oxide moieties. X-ray powder diffraction studies show that upon desolvation, compound **2** maintains its original ladder framework.

Keywords: co-ordination chemistry · co-ordination polymers · crystal engineering · interpenetration · lanthanides

Introduction

Many examples of rationally designed poly-dimensional co-ordination networks have been constructed by using the concepts of crystal engineering.[1] The majority of studies thus far have used bridging ligands such as 4,4′-bipyridine and its analogues containing two or more 4-pyridyl donor units bound to transition metal ions.[2] Although a number of examples have appeared recently on the construction of lanthanide open frameworks by employing O-donor bridging ligands such as sulfoxides,[3] carboxylates,[4] pyridones and lactams,[5, 6] f-block metal ions have received comparatively less attention than d-block cations. Recently, our work on the application of 4,4′-bipyridine-*N*,*N*′-dioxide (L) has revealed that this ligand plays the same important role as its genitor compound 4,4′-bipyridine in both lanthanide and transition metal co-ordination polymers. These studies have resulted in a family of extended assemblies including sheets of 4.8^2 topology, interpenetrating CdSO$_4$-like nets[7] and unusual five-,[8] six-, seven- and eight-connected topologies.[9] We have also shown different connection modes of this ligand, including co-ordination, hydrogen bonding, or $\pi - \pi$ stacking in its d-block metal complexes.[10] The effect of different solvents on the formation of co-ordination polymers is readily appreciated, but systematic studies of their role are still scarce.[11–13] In our current studies on the complexation of 4,4′-bipyridine-*N*,*N*′-dioxide by lanthanide ions both the ligand and metal salts are readily soluble in MeOH and sparingly soluble in halogenated solvents, and we have employed different solvent mixtures of MeOH and halogenated solvents in our attempts to influence co-ordination polymer formation. We report herein the syntheses, characterisation and crystal structures of five terbium co-ordination polymers $[Tb(L)(CH_3OH)(NO_3)_3]_\infty$ (**1**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot CH_2Cl_2\}_\infty$ (**2**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot CH_3OH \cdot 0.8H_2O\}_\infty$ (**3**), $\{[Tb(L)_{1.5}(NO_3)_3] \cdot 0.4C_2Cl_4 \cdot 0.8CH_3OH\}_\infty$ (**4**) and $[Tb(L)_2(NO_3)_3]_\infty$ (**5**), which were obtained by tuning solvent mixtures.

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Results and Discussion

Co-ordination polymer synthesis: Four distinct techniques were used to prepare and crystallise compounds **1**–**5**. Method A involved dissolving Tb(NO₃)₃ in MeOH and then carefully mixing this solution with a methanolic solution of the ligand, which in general afforded crystalline products over a period of days. Method B consisted of placing Tb(NO₃)₃ at the bottom of a glass vial and covering it with a halogenated anti-solvent. Over this protective layer a solution of the ligand in MeOH was
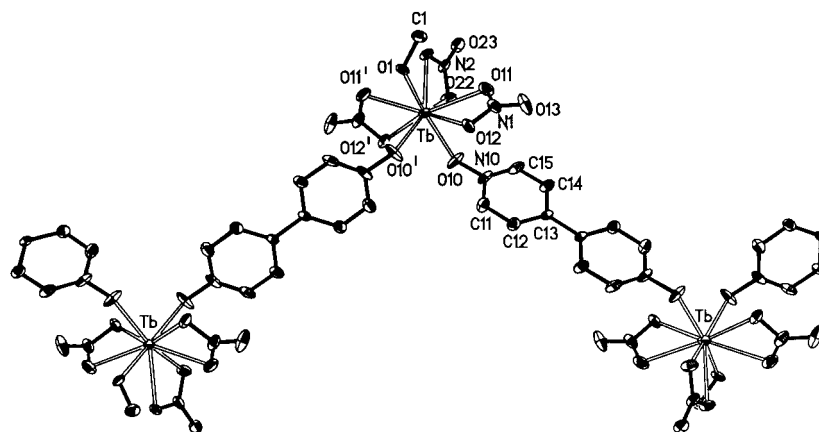

Figure 1. A view of the zig-zag structure of compound **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Tb–O1 2.320(10), Tb–O21 2.519(4), Tb–O10 2.271(2), Tb–O22 2.546(10), Tb–O11 2.458(3), O10–N10 1.334(3), Tb–O12 2.471(3); O11-Tb-O12 51.8(1), O21-Tb-O22 50.4(2), O10-Tb-O10^i 87.1(2), N10-O10-Tb 131.4(2). Symmetry code: i: $-x, y, 0.5 - z$.

layered and slow diffusion of the two solvents afforded what we term a "diffusion solvent mixture". Crystals of the product formed with concomitant dissolution of the solid Tb(NO₃)₃ over a period of approximately two weeks. Method C used what we term a "pre-mixed solvent". The method consists of dissolving separately both Tb(NO₃)₃ and the ligand in a pre-mixed solvent comprising MeOH and a halogenated solvent. These two solutions were then carefully mixed, resulting in a clear solution that precipitated a microcrystalline solid within hours. Method D employed a U-tube with a buffer of neat halogenated solvent filling its central segment. This separates methanolic solutions of Tb(NO₃)₃ and the ligand, which are positioned in different arms of the U-tube. The product crystallises in the central portion of the U-tube over a period of weeks. A similar procedure has been described previously by Khasanov.[14]

Compounds **1**, **2** and **4** were obtained by the reaction of solid Tb(NO₃)₃ with L using a "diffusion solvent mixture" of MeOH and a halogenated anti-solvent (CHCl₃ or CHCl₂CHCl₂ for **1**, CH₂Cl₂ for **2**, C₂Cl₄ for **4**) as in method B. The main function of the halogenated solvent is to slow the rate of the reaction and hence crystallisation. However, we also observed more profound effects for "diffusion solvent mixtures" formed from methanol and different halogenated solvents. Compounds **3** and **5** were obtained from mixed methanolic solutions of Tb(NO₃)₃ and L (method A) and this is the most commonly used method of co-ordination polymer synthesis.

Structural characterisation of 1–5: Compounds **1**–**5** were investigated by single-crystal X-ray analysis, which determined that these materials have polymeric structures based on networks of nine co-ordinate terbium(III) centres with distorted tricapped trigonal-prismatic geometries. Selected bond lengths and angles are given in figure captions.

The structure of **1** exhibits a three-dimensional framework built from zig-zag chains (Figure 1) joined by inter-chain hydrogen bonds. Terbium(III) centres in **1** lie on crystallographic twofold axes and in a nona-co-ordinate TbO₉ environment with one oxygen atom from each of two different molecules of L, one from a co-ordinated methanol, and six

others from three bidentate nitrate anions. The two 4,4′-bipyridine-N,N′-dioxide ligands form a "V-joint" at the terbium(III) centres, causing the chain to undulate with a Tb···Tb···Tb angle of 99.7°. Neighbouring terbium centres in the chain are separated by the ligand at a distance of about 13.2 Å, while the shortest interchain Tb···Tb separation in the crystal is 8.0 Å.

Figure 2a is a schematic representation of the overall framework formed by the co-ordination polymers of **1**. The
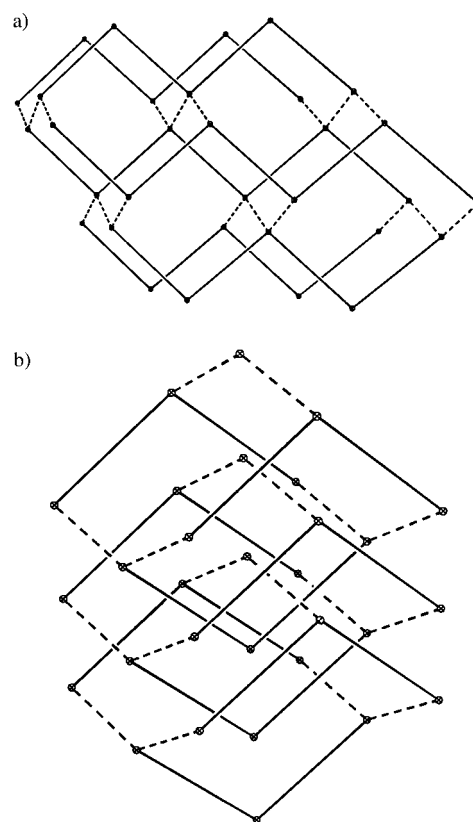

Figure 2. a) Schematic representation of the framework formed from zigzag chains (full lines) by hydrogen bonds (dashed lines) in **1**; b) schematic representation of the threefold interpenetration of the diamondoid framework in **1**.

dashed lines represent the hydrogen bonding interactions between the co-ordinated MeOH and a co-ordinated nitrate group on an adjacent chain. The O ··· O distance of 2.74 Å and O−H ··· O angle of 177° indicate comparatively strong inter-chain interactions. With the aid of these contacts each terbium(III) centre can be considered to be a four-connected node and the network forms a three-dimensional (3D) structure of 6^6 topology. Although the node geometry deviates from tetrahedral, the overall structure has indeed the same topology as a superdiamondoid, or adamantoid, array. When viewed along the c direction, the structure is seen to contain large channels (about 10×10 Å), which are occupied by two other chemically identical interpenetrating frameworks resulting in a close-packed structure (Figure 2b). Threefold interpenetrating co-ordination networks based on four-connected centres are scarce to date. Previous examples of threefold interpenetrating diamondoid nets, including $[\{Cu(diazapyrene)_2\}PF_6\}_{\infty}$,[15] $\{[Cu(dmtpn)_2](X)(dmtpn)-(THF)\}_{\infty}$ (X = BF$_4$, ClO$_4$; dmtpn = 2,5-dimethylterephthalo-nitrile),[16] $[Cu(CN)(4\text{-cyanopyridine})]_{\infty}$,[17] $Ag_2\{OOC(CH_2)-COO\}]_{\infty}$,[18] and $\{[Cd(mea)(dahxn)\{Ni(CN)_4\}] \cdot H_2O\}_{\infty}$[19] are all constructed from d-metal junctions. To our knowledge, no example of threefold interpenetrating networks has been reported for lanthanide co-ordination polymers,[20] although a few examples of twofold interpenetrating structures have been reported.[4a, 21]

The terbium(III) centres in **2** lie in a distorted tricapped trigonal prismatic nona-co-ordinate environment. As shown in Figure 3, the three ligands L form a "T-joint" at the
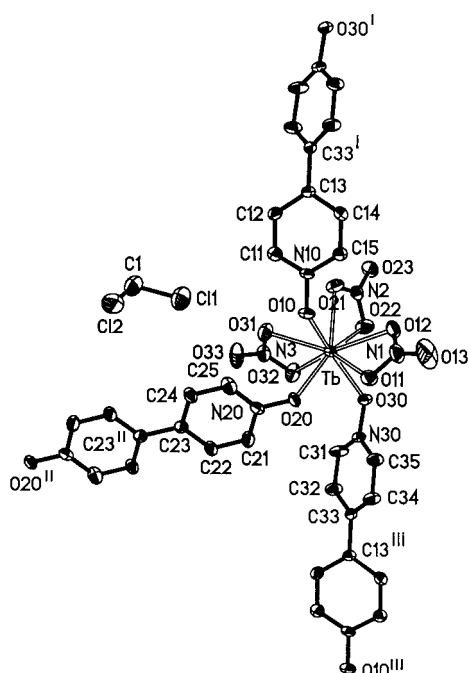
Figure 3. Asymmetric unit and labelling scheme for compound **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Tb−O11 2.495(7), Tb−O12 2.452(6), Tb−O21 2.473(6), Tb−O22 2.489(7), Tb−O31 2.489(7), Tb-O32 2.486(6), Tb−O10 2.327(6), Tb−O20 2.317(6), Tb−O30 2.299(6), O10−N10 1.348(8), O20−N20 1.334(8), O30−N30 1.352(8); O10-Tb-O20 83.4(2), O20-Tb-O30 85.9(2), O11-Tb-O12 51.6(2), O21-Tb-O22 50.6(2), O31-Tb-O32 50.8(2), N10-O10-Tb 125.8(4), N20-O20-Tb 128.5(5), N30-O30-Tb 129.2(5). Symmetry codes: i: x, y, 1 + z; ii: 2 − x, − y, 1 − z; iii: x, y, − 1 + z.

terbium(III) centres, the remaining co-ordination sites being occupied by three bidentate nitrate anionic ligands. Thus, **2** has an infinite molecular ladder structure, which involves a 44-membered parallelogram substructure with an inner angle of 72.3°. The parallelogram subunit consists of four ligands L and four terbium(III) ions, with each ligand bridging two terbium(III) centres. The large channels formed by superposition of ladders (Figure 4a) leave residual free space (about 17.0% of
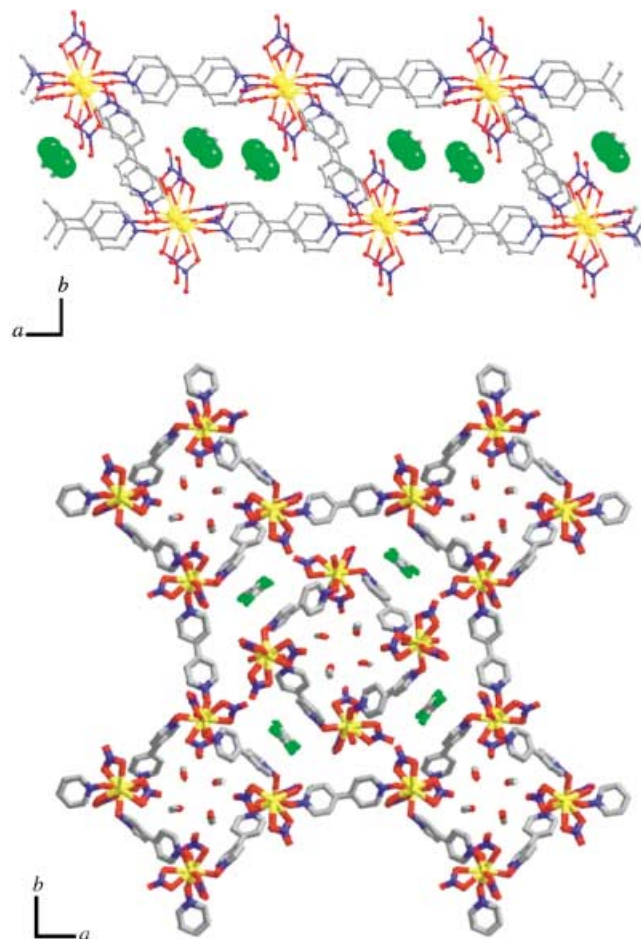
Figure 4. a) Channels formed by superposition of ladders of **2**, with guest CH$_2$Cl$_2$ molecules highlighted (above). b) Channels formed by super-position of 2D 4.8^2 nets in **4** accommodate the tetrachloroethylene and methanol solvent molecules (below). Hydrogen atoms are omitted for clarity.

the unit cell volume[22]) permitting the inclusion of small molecules, CH$_2$Cl$_2$ in the case of **2**. The ladder motif is known for d-block metals complexes such as $[Co_2(NO_3)_4(1,2\text{-bis(4-pyri-dyl)ethyne})_3]_{\infty}$,[23] $[Cd_2(NO_3)_4(1,2\text{-bis(4-pyridyl)ethane})_3]_{\infty}$,[24] $[Co_2(NO_3)_4(1,2\text{-bis(4-pyridyl)ethane})_3]_{\infty}$,[11] $[Co_2(NO_3)_4(4,4'\text{-bipyridine})_3]_{\infty}$,[25] $[Cd_2(NO_3)_4(1,4\text{-bis(4-methylenepyridyl)ben-zene})_3]_{\infty}$,[26] $[M_2(NO_3)_4(3,6\text{-bis(pyridin-3-yl)-1,2,4,5-tetra-zine})_3]_{\infty}$ (M = Cd, Zn)[12] and $\{[Cu_2(MeCN)_2(1,4\text{-bis(4-pyridyl)butadiyne})_3]PF_6\}_{\infty}$.[27] Most of these polymers are based upon pseudo-octahedral or pentagonal-bipyramidal metal centres that generate what may be termed a flat ladder with all linking ligands coplanar. In the last case,[27] however, the tetrahedral Cu^I centres allow the ladder to undulate. A few examples of ladder structures generated from f-block or a

combination of d-block and f-block metals are also known such as those found in $[Ln(H_2O)_x(C_2O_4)\{O(CH_2CO_2)_2\}_2]_\infty$[28] and $\{Ln_2[Cu(opba)]_3\}_\infty$[29] (Ln = lanthanide ion, opba = *ortho*-phenylenebis(oxamato)), all of which are generated by using oxalate or carboxylate chelating ligands. The present structure represents the first lanthanide-based molecular ladder with a homonuclear co-ordination sphere made from a nonchelating bridging ligand.

The terbium(III) ions in **3** and **4** are nine co-ordinate with six oxygen donors from three bidentate nitrates and the rest from three ligands L (Figure 5). Compounds **3** and **4** form similar
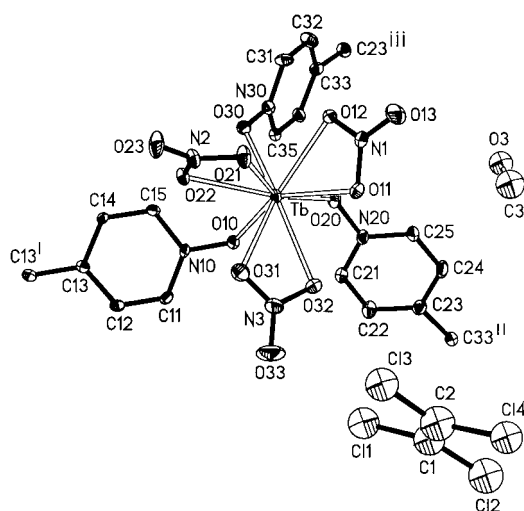

Figure 5. Asymmetric unit and labelling scheme for **4**. Hydrogen atoms are omitted for clarity. Compound **3** has similar structure except for the solvent molecules. Selected bond lengths [Å] and angles [°] for **3**: Tb−O10 2.313(14), Tb−O20 2.249(13), Tb−O30 2.344(11), Tb−O11 2.439(14), Tb−O12 2.504(13), Tb−O21 2.468(14), Tb−O22 2.496(12), Tb−O31 2.452(14), Tb−O32 2.511(12), O10−N10 1.34(2), O20−N20 1.31(2), O30−N30 1.34(2); O10-Tb-O30 81.9(5), O20-Tb-O30 84.2(5), O20-Tb-O10 78.1(5), O11-Tb-O12 52.5(4), O21-Tb-O22 51.5(4), O31-Tb-O32 52.5(5), N10-O10-Tb 129.4(11), N20-O20-Tb 133.1(11), N30-O30-Tb 122.8(10). Selected bond lengths [Å] and angles [°] for **4**: Tb−O10 2.314(3), Tb−O20 2.260(3), Tb−O30 2.341(3), Tb−O11 2.451(3), Tb−O12 2.483(3), Tb−O21 2.472(3), Tb−O22 2.494(3), Tb−O31 2.450(4), Tb−O32 2.486(3), C1−Cl1 1.732(3), C1−Cl2 1.721(4), C2−Cl3 1.725(4), C2−Cl4 1.727(4), O10−N10 1.321(5), O20−N20 1.334(5), O30−N30 1.332(5); O10-Tb-O30 81.89(11), O20-Tb-O30 83.72(11), O20-Tb-O10 78.75(12), O11-Tb-O12 52.04(10), O21-Tb-O22 51.44(11), O31-Tb-O32 51.36(12), N10-O10-Tb 130.2(3), N20-O20-Tb 131.6(3), N30-O30-Tb 124.5(2). Symmetry codes: *i*: $1-x, -y, z$; *ii*: $-y, x, -1-z$; *iii*: $y, -x, -1-z$.

2D sheets of 4.8^2 topology, in which the three-connected nodes are shared by one square unit and two octagonal units (Scheme 1). The same structural motif is observed for $\{[Er(L)_{1.5}(NO_3)_3]\cdot CH_3OH\}_\infty$.[7] The structure thus formed contains large cavities with the octagonal unit, comprising eight metal ions and eight ligands, having a diameter of about 2.6 nm. The structure does not exhibit interpenetration but rather this large cavity is occupied by a four-membered ring of metal atoms from a parallel adjacent layer. Although **3** and **4** have the same 4.8^2 network structures, they act as hosts for different solvent molecules. Two kinds of channel are generated along the crystallographic *c* axis (perpendicular to the plane of the 4.8^2 net) by the superposition of these 2D
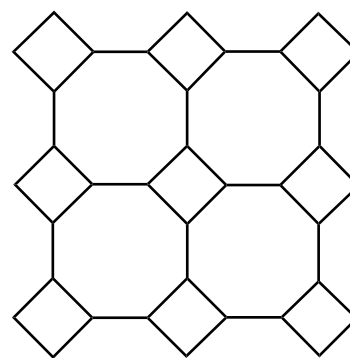
Scheme 1.

nets; one is inside the square-shaped unit (dimensions about 10×10 Å), which includes MeOH molecules, while the other is positioned between squares from adjacent layers and is occupied by water molecules in the case of **3** and tetrachloroethylene molecules in the case of **4** (Figure 4b).

The terbium(III) ions in **5** are nine co-ordinate, with six oxygen donors from three bidentate nitrates and three others from three 4,4′-bipyridine-*N,N*′-dioxide ligands. These 4,4′-bipyridine-*N,N*′-dioxide ligands form a distorted T-shaped node at the terbium(III) centres (Figure 6). Unlike the T-shaped nodes adopted by $M(NO_3)_2$ (M = Co, Ni, Zn, Cd) building blocks which form molecular ladder,[23–26] brickwall,[25, 30] herringbone,[23, 24, 31] tongue-and-groove[32] or three-dimensional frameworks,[33] the terbium(III) centres in **5** adopt a linear polymeric structure with pendant terminal ligands from alternate nodes lying on opposite sides of the one-dimensional chain (Figure 7). This results in a layered polymeric structure of (6,3) topology for **5**, formed by means of an electrostatic interaction between *N*-oxide moieties (Figure 7). Similarly shaped nodes in **2**, **3** and **4** generate ladder or 4.8^2 network structures. For all previous lanthanide co-ordination compounds of L this ligand has adopted a bridging mode, although examples of pendant L molecules have been found for d-block metal complexes.[10]

As *N*-oxide groups have formal partial negative and positive charges on the oxygen and nitrogen atoms, respectively, it is reasonable to consider an electrostatic interaction between two *N*-oxide groups as shown in Scheme 2. To our surprise, no examples of such an interaction have been reported in the Cambridge Structural Database (CSD) for either organic or organometallic compounds. The shortest intermolecular N···O distance of 3.88 Å was identified in $[Co(nicotinato-N-oxide)_2(H_2O)_4]$,[34] but no electrostatic *N*-oxide interaction was invoked and rather *N*-oxide···H_2O hydrogen bonding was emphasised. In compound **5** the intermolecular N···O distance O40···N40iii of 2.931(2) Å (symmetry code *iii*: $-y, -y, -z$) (Figure 6), is considerably shorter than the spacings associated with aromatic $\pi-\pi$ interactions[35] and indicates the existence of an electrostatic interaction between two *N*-oxide groups. Taking this interaction into account, a (6,3) plane net is formed by **5** (Figure 7). The identification of this electrostatic interaction between two *N*-oxide groups offers a potential new strategy for crystal engineering.
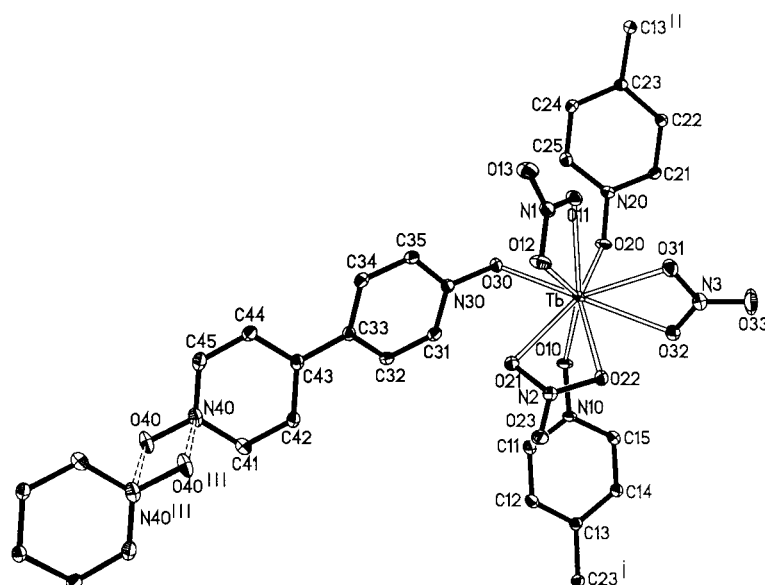
Figure 6. View showing the Tb co-ordination sphere and labelling scheme for **5**. The intermolecular *N*-oxide electrostatic interaction is shown as double dashed lines. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **5**: Tb−O10 2.291(2), Tb−O20 2.294(2), Tb−O30 2.325(2), Tb−O11 2.535(2), Tb−O12 2.501(2), Tb−O21 2.548(2), Tb−O22 2.457(2), Tb−O31 2.451(2), Tb−O32 2.516(2), O10−N10 1.337(2), O20−N20 1.335(2), O30−N30 1.339(2), O40−N40 1.298(2); O10-Tb-O30 83.93(6), O10-Tb-O20 87.95(6), O20-Tb-O30 78.23(5), O11-Tb-O12 50.73(5), O21−Tb−O22 51.33(5), O31−Tb−O32 51.66(6), N10−O10−Tb 136.80(14), N20−O20−Tb 132.13(13), N30-O30-Tb 125.16(12). Symmetry codes: *i*: −1 + *x*, 1.5 − *y*, −0.5 + *z*; *ii*: 1 + *x*, 1.5 − *y*, 0.5 + *z*; *iii*: −*x*, −*y*, −*z*.
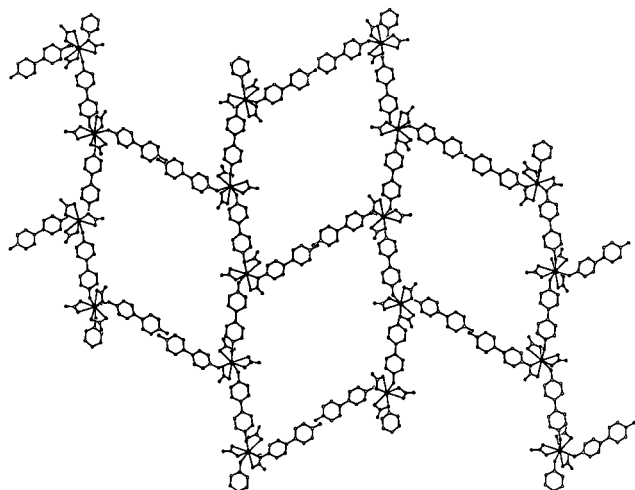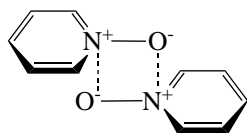

Figure 7. (6, 3) nets formed through *N*-oxide electrostatic interactions in **5**.

Scheme 2.

Comparison of methods of co-ordination polymer synthesis and crystal growth: Diffusion solvent mixtures have been widely applied for crystal growth. A traditional synthetic route is the successive layering of the methanolic metal salt solution over a halogenated solvent solution of the ligand.[1,2] However, in the case of the current system, both 4,4′-bipyridine-*N,N′*-dioxide and lanthanide salts are readily

soluble in MeOH and sparingly soluble in halogenated solvents. Based on this, a synthetic strategy using solid metal salt was applied to produce co-ordination polymers. The ligand was dissolved in methanol and layered over a solvent, such as CH₂Cl₂, which does not dissolve the metal salt but covers the solid metal salt on the bottom of the crystallisation vessel. Because the reactants are separated, they can only combine slowly and as diffusion occurs, a solvent mixture with variable composition gradually forms at the interface and slowly dissolves the metal salt. The concentration of both ligand and metal ion is believed to be appropriate when they meet in such a "diffusion solvent mixture" and this is beneficial for the growth of high quality crystals. This is a simple, easily controlled, efficient and useful synthetic method, which could easily be applied to other organic ligands with the same features as 4,4′-bipyridine-*N,N′*-dioxide. The greatest advantage of this strategy that we have observed in our system is that the isolated products are of a single phase, as confirmed by X-ray powder diffraction. Using this strategy, we obtained the products in large amounts while using only small amounts of solvent, unlike traditional crystal growth by solvent diffusion, in which the reactants must be in very low concentrations, necessitating the use of large volumes of solvent in order to obtain greater quantities of product. Secondly, the composition and structure of the products is almost independent of the reactant ratio but depends rather on the properties of the halogenated antisolvent. Regardless of the amount of solid metal salt used in the reaction, the critical metal ion and ligand concentrations in the diffusion solvent mixture are always the same. Because of the continuous supply of metal ions from the solid salt, the concentration of the reactants will remain constant for a considerable period of time, unlike the situation in traditional solvent diffusion processes. By using different combinations of solvents in the diffusion solvent mixture, the position of crystal growth varies: in some cases crystals appear on the bottom of the vial and in others on the vessel wall. This suggests that the different solvent mixtures affect not only metal ion and ligand transportation but also the process of product and crystal formation. For comparison, normal solvent mixtures (solvent mixtures fully dispersed prior to crystallisation) of the same proportions of solvent were used to dissolve both the metal salt and ligand separately and then mixed for the synthesis of **1** and **2**. In both cases a mixture of products was obtained. Finally, in some instances, such as the synthesis of **4**, normal solvent mixtures with tetrachloro-

ethylene as the anti-solvent are difficult to obtain because of solvent immiscibility, and the solid salt method is the only viable technique. The synthesis of compounds **2** and **4**, which cocrystallise with the anti-solvent, and the structural diversity of **1**, **2**, **4** and **5** illustrate the significance of this strategy.

Compounds **1**, **2** and **4** have also been obtained in small amounts and low yields by means of method D, although for the present system we tend to use method B since it is comparatively simple and flexible.

Stability of {[Tb(L)$_{1.5}$(NO$_3$)$_3$] · CH$_2$Cl$_2$}$_\infty$ (2) to guest removal: Despite the inclusion of volatile CH$_2$Cl$_2$ solvent molecules, crystals of **2** are stable with respect to solvent loss when exposed to air, as confirmed by elemental analyses recorded for samples following many days of exposure to air. However, the CH$_2$Cl$_2$ molecules can be removed by heating in vacuo. Thermogravimetric analysis in static air shows that the compound loses weight over a temperature range of 90 – 150°C, the total weight loss of 11.5% corresponding to one CH$_2$Cl$_2$ molecule per metal centre, consistent with the elemental analysis and empirical formula obtained by X-ray crystallography. Powder X-ray diffraction patterns indicate that the framework in compound **2** is maintained after removal of the guest molecules, although the observed broadening of the PXRD peaks indicates some loss of crystallinity.

Conclusion

We have reported the structures of five co-ordination polymers generated from Tb(NO$_3$)$_3$ and the ligand 4,4′-bipyridine-*N,N*′-dioxide, L, in different solvent mixtures. The predominant feature of the results reported here, together with those we have previously published for co-ordination polymers of L with Sm(NO$_3$)$_3$ or Er(NO$_3$)$_3$,[7] is the exciting diversity of solid-state structures produced by varying the metal ion and solvent mixtures. In these lanthanide nitrate compounds the nitrate anions are comparable in co-ordinative ability with the 4,4′-bipyridine-*N,N*′-dioxide ligand. Thus, in all cases the nitrates act as chelating ligands, occupying six co-ordination sites and leaving the remaining sites available for *N*-oxide co-ordination. For early lanthanide ions, the four remaining ligand sites lead to four-connected structural nodes and CdSO$_4$-like frameworks. For heavier lanthanide ions three-connected nodes are observed, which lead to molecular ladders and (6,3) and 4.8^2 nets. Although the "diffusion solvent mixture" method has been widely applied in chemical synthesis and crystal growth, the strategy described in this study of using metal salts has been shown to be a simple and effective method for the construction of lanthanide networks and for crystal engineering.

Experimental Section

General: All chemicals (Aldrich) were reagent grade and were used as received. Microanalyses (C, H, N and Cl) were performed by the University of Nottingham School of Chemistry Microanalytical Service. IR spectra were recorded as KBr discs using a Nicolet Avatar 360 FT-IR spectrometer over the 400 – 4000 cm^{-1} range. Powder X-ray diffraction (PXRD) data

were collected on a Philips X'pert θ-2θ diffractometer with Cu$_{K\alpha}$ radiation in a 2θ range of 5 – 80°. Thermogravimetric analysis was carried out on a Rheometric Scientific STA 1500H thermal analyzer. The samples of about 50 mg were loaded into platinum crucibles and heated at a rate of 3°C min^{-1} from room temperature to 250°C in static air.

General synthetic procedures of complex synthesis, **Method A**: Metal nitrate hydrate (ca. 0.05 mmol) was dissolved in MeOH (ca. 10 mL) and carefully mixed with a MeOH solution (ca. 10 mL) of L · hydrate (in the specified ratio with metal salt), affording crystalline products in a few days.

Method B: "Diffusion solvent mixture": solid metal nitrate hydrate (ca. 0.05 mmol) placed at the bottom of a glass vial was covered with a halogenated anti-solvent (ca. 10 mL), over which a solution of L · hydrate (22 mg, 0.10 mmol) in MeOH (ca. 10 mL) was layered. Over a period of approximately two weeks, the solid metal salts gradually dissolved in the solvent mixture with concomitant formation of crystals of the product on the wall of the vial.

Method C: "Normal solvent mixture": The metal salt (ca. 0.10 mmol) was dissolved in a mixture of MeOH/halogenated solvent (1:1) (10 mL) and carefully added dropwise into a solution of L · hydrate (ca. 0.15 mmol) in the same pre-mixed solvent mixture (10 mL), resulting first in a clear solution and then microcrystalline solid within hours.

Method D: A halogenated solvent (4 mL) was placed in the central segment of a U-tube. This halogenated buffer separates metal nitrate and ligand (each ca. 0.01 mmol) in MeOH (2 mL). The product crystallises in the central portion of the U-tube over a period of weeks.

Preparation of [Tb(L)(CH$_3$OH)(NO$_3$)$_3$]$_\infty$ (1): Compound **1** was produced using method B with a metal:ligand ratio of 1:1.5 as a single phase, confirmed by powder X-ray diffraction (PXRD). The anti-solvent used was either CHCl$_3$ or 1,1,2,2-tetrachloroethane. The yield of **1** was about 55%. Using method C for this reaction (normal solvent mixture MeOH/CHCl$_3$ or MeOH/1,1,2,2-tetrachloroethane) yields a product mixture containing **1**, **3**, **5** and other unidentified phases, confirmed by PXRD. Single phase **1** was also obtained by using method D. IR (KBr disc): 1632m, 1506s, 1478s, 1384s, 1332s, 1278m, 1230s, 1183m, 1019m, 842s, 567m cm^{-1}; elemental analysis calcd (%) for C$_{11}$H$_{12}$N$_5$O$_{12}$Tb (565.18): C 23.38, H 2.14, N 12.39; found C 23.09, H 2.00, N 12.75.

Preparation of {[Tb(L)$_{1.5}$(NO$_3$)$_3$] · CH$_2$Cl$_2$}$_\infty$ (2): Single phase **2**, confirmed by PXRD, was produced employing method B and a metal:ligand ratio of 1:1.5 with CH$_2$Cl$_2$ as the anti-solvent. The yield of **2** was about 60%. This solvated compound is stable, maintaining crystalline morphology and constant chemical analyses after exposure to air for five days. Using method C produced microcrystalline precipitate in minutes. PXRD indicated the product contains **1**, **2**, **3** and a small proportion of a fourth unidentified phase. Compound **2** was also obtained as a single phase by method D. IR (KBr pellet): 1638m, 1473s, 1384s, 1312s, 1231s, 1187m, 1033s, 841s, 562m cm^{-1}; elemental analysis calcd (%) for C$_{16}$H$_{14}$Cl$_2$N$_6$O$_{12}$Tb (712.15): C 26.98, H 1.98, Cl 9.96, N 11.80; found C 26.96, H 1.87, Cl 9.78, N 11.95.

Preparation of {[Tb(L)$_{1.5}$(NO$_3$)$_3$] · CH$_3$OH · 0.8H$_2$O}$_\infty$ (3) and [Tb(L)$_2$(NO$_3$)$_3$] (5): Using method A (metal:ligand ratio 1:1.5) initially gave an opaque solution, which then became clear and produced colourless lath-shaped crystals (**3**) and pale yellow block crystals (**5**) in two days. Crystals of **3** and **5** were separated mechanically. The yield was about 30% for **3** and 35% for **5**.

3: IR (KBr disc): 1635m, 1474s, 1384s, 1313m, 1229s, 1185m, 1032s, 841s, 561m cm^{-1}; elemental analysis calcd (%) for C$_{16}$H$_{17.6}$N$_6$O$_{13.8}$Tb (673.68): C 28.53, H 2.63, N 12.48; found: C 27.70, H 2.22, N 12.40.

5: IR (KBr disc): 1636m, 1475s, 1384s, 1312m, 1231s, 1187m, 1033s, 840s, 564m cm^{-1}; elemental analysis calcd (%) for C$_{20}$H$_{16}$N$_7$O$_{13}$Tb (721.32): C 33.30, H 2.24, N 13.59; found: C 33.14, H 2.20, N 13.33.

Preparation of {[Tb(L)$_{1.5}$(NO$_3$)$_3$] · 0.4C$_2$Cl$_4$ · 0.8CH$_3$OH}$_\infty$ (4): Compound **4** was produced as a single phase, confirmed by PXRD, using method B in metal:ligand ratio of 1:1.5 and with tetrachloroethylene as anti-solvent. The yield of **4** was about 50%. Compound **4** was also obtained as a single phase by method D. IR (KBr disc): 1646m, 1475s, 1384s, 1314m, 1227s, 1181m, 1032s, 840s, 560m cm^{-1}; elemental analysis calcd (%) for C$_{16.6}$H$_{15.2}$Cl$_{1.6}$N$_6$O$_{12.8}$Tb (719.19): C 27.72, H 2.13, N 11.69, Cl 7.89; found: C 26.70, H 2.03, N 11.71, Cl 8.14.

Removal of guest CH_2Cl_2 molecules from 2: To evaluate the removal of the CH_2Cl_2 guest molecules from $\{[Tb(L)_{1.5}(NO_3)_3] \cdot CH_2Cl_2\}_\infty$ **2**, a PXRD pattern was measured for the bulk product. The program POWDERCELL 2.3[36] was used to refine the cell parameters for the bulk product: triclinic, $a = 8.084$, $b = 11.761$, $c = 13.073$ Å, $\alpha = 86.78$, $\beta = 79.55$, $\gamma = 78.78°$, $V = 1198.7$ Å^3. A freshly prepared sample was heated at 100°C under reduced pressure (1×10^{-3} Torr) for 3 h. Elemental analysis of the desolvated compound shows a chlorine content of 0.3% and suggests a formulation of $[Tb(L)_{1.5}(NO_3)_3] \cdot H_2O$, the water component presumably arising from absorbed atmospheric moisture and reflecting the high absorption activity of desolvated **2**. Elemental analysis calcd (%) for $C_{15}H_{14}N_6O_{13}Tb$: C 27.92, H 2.19, N 13.02; found: C 27.89, H 1.96, N 12.90. Compared with that of **2**, the PXRD pattern of the desolvated compound is considerably broadened with the cell parameters being refined[36] as: triclinic, $a = 8.076$, $b = 11.746$, $c = 13.066$ Å, $\alpha = 86.77$, $\beta = 79.61$, $\gamma = 78.72°$ $V = 1195.3$ Å^3.

X-ray crystallography: Diffraction data for **2** were collected at 298 K on a Stoë Stadi-4 four-circle diffractometer, graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\omega - \theta$ scans. An absorption correction based upon ψ scans was applied to the data. Diffraction data for **1**, **3**, **4** and **5** were collected at 150 K on a Bruker SMART1000 CCD diffractometer equipped with an Oxford Cryosystems open-flow cryostat,[37] employing graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and ω scans. An absorption correction based upon symmetry equivalent reflections was applied to the data. The structures were solved using direct methods[38] and all non-hydrogen atoms were located by using subsequent difference-Fourier methods.[39] Hydrogen atoms on pyridyl rings were placed in calculated positions and refined in riding mode, while those on oxygen atoms were found in the difference-Fourier map and then refined as part of rigid rotating groups. Most of the non-hydrogen atoms were refined with anisotropic displacement parameters. A disorder model with a methanol and a nitrate group sharing two sites (each having half occupancy) was applied to compound **1**. Disorder models with solvent molecules of partial occupancy were used in the refinement of **3** and **4**. Further crystallographic details are given in Table 1.

CCDC-170540 (**1**), CCDC-170541 (**2**), CCDC-170543 (**3**), CCDC-170542 (**4**), and CCDC-170544 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

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Table 1. Crystal data and details of structure solution and refinement for compounds **1**, **2**, **3**, **4** and **5**.

	1	2	3	4	5
formula	$C_{11}H_{12}N_5O_{12}Tb$	$C_{16}H_{14}Cl_2N_6O_{12}Tb$	$C_{16}H_{17.6}N_6O_{13.8}Tb$	$C_{16.6}H_{15.2}Cl_{1.6}N_6O_{12.8}Tb$	$C_{20}H_{16}N_7O_{13}Tb$
crystal system	monoclinic	triclinic	tetragonal	tetragonal	monoclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{4}2_1/c$	$P\bar{4}2_1/c$	$P2_1/c$
a [Å]	15.228(2)	8.086(2)	26.304(6)	26.154(4)	9.3944(6)
b [Å]	8.3001(9)	11.769(3)			14.6498(9)
c [Å]	13.996(2)	13.078(2)	7.580(2)	7.5828(11)	17.2874(10)
α [°]		86.80(2)			
β [°]	92.705(3)	79.52(2)			90.577(1)
γ [°]		78.79(2)			
V [Å^3]	1767.0(6)	1200.2(5)	5245(3)	5187(2)	2379.1(4)
Z	4	2	8	8	4
ρ_{calcd} [g cm^{-3}]	2.124	1.971	1.706	1.842	2.014
μ(Mo$_{K\alpha}$) [cm^{-1}]	4.080	3.242	2.770	2.964	3.06
measured data	5778	8855	15393	21785	14992
unique data	2235	4687	5915	6339	5792
observed data ($\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$)	2093	3829	3232	5199	5575
R, R'	0.027, 0.061	0.053, 0.109	0.088, 0.201	0.043, 0.098	0.021, 0.051

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