Anion Control over Interpenetration and Framework Topology in Coordination Networks Based on Homoleptic Six-Connected Scandium Nodes

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Abstract: Reaction of ScX_3 ($X = NO_3^-$, $CF_3SO_3^-$, ClO_4^-) with 4,4′-bipyridine-*N,N*′-dioxide (L) affords topologically distinct six-connected three-dimensional coordination frameworks, $\{[Sc(L)_3](NO_3)_3\}_\infty$ (**1**), $\{[Sc(L)_3](CF_3SO_3)_3(CH_3OH)_{2.7}(H_2O)_3\}_\infty$ (**2**), $\{[Sc(L)_3](ClO_4)_3\}_\infty$ (**3**) and $\{[Sc(L)_4(H_2O)_2](ClO_4)_3\}_\infty$ (**4**). Compounds **1, 2** and **3** are networks based on octahedrally co-ordinated ScO_6 centres bound through six oxygen atoms from six separate *N*-oxide ligands L. Compounds **1** and **3** are doubly interpenetrated and have α-polonium-type structures of $4^{12}6^3$ topology based upon three intersecting (4,4) nets. The structure of **2** is unusual and shows parallel, co-planar layers of (4,4) nets connected in a criss-crossed fashion to afford a new 4^86^68 topology. In **4** only four ligands L bind to each Sc^{III} centre with two additional water molecules bridging metal nodes. Significantly, the bridges formed by L do not sit in a plane and if connections through L are considered alone the resultant structure is a diamondoid array typically based upon a *tetrahedral* connecting node at Sc. Five interpenetrating diamondoid networks are observed that are cross-bridged by water molecules to form a single three-dimensional array of 4^86^7 topology. Compound **4** can also be viewed as incorporating two intersecting (4,4) grids based upon two ligands L and two bridging waters. Thus, variation of anion, solvent and conditions critically affects the structures of products formed, and the series of polymers reported herein illustrates how tectons based upon (4,4) grids can be combined and distorted to form non-NaCl topologies and even cross-bridged, multiply interpenetrated diamondoid materials. Both compounds **2** and **4** represent unusual examples of self-penetrated coordination frameworks.

Keywords: coordination polymers · N ligands · scandium · self-penetration · supramolecular chemistry

Introduction

The construction of inorganic networks through crystal engineering has been the subject of much interest in recent years[1] partly because of their potential application as functional materials.[2] Of the more common transition-metal geometries, linear metal centres often afford chains,[3] square-planar cations (4,4) square-grid structures[4] and tetrahedral ions diamondoid networks.[5] Networks formed from octahedral connecting nodes are far less common[6–12] despite the common occurrence of octahedral transition-metal complexes. Six-connected network structures, in their simplest form, consist of octahedral centres linked together in a cubic network of squares (that is 3D space tessellated by cubes). Of the previously reported six-connected coordination polymers, only a few adopt the α-polonium-type structure. These include $[Ag(pyrazine)_3](SbF_6)$,[6] $\{[Sc(O_2CC{\equiv}CH)_3]\}_\infty$,[7] the doubly interpenetrated $\{[Mn(N,N'\text{-butylenebisimidazole})_3](BF_4)_3\}_\infty$,[8] non-interpenetrated $\{[Co(HMBA)]_3(CoCl_4)\}_\infty$ and $\{[Mn(HMBA)_3](MnBr_4)\}_\infty$ (HMBA = hexamethylenebis(acetamide)[9] and the family of cyanide-bridged frameworks related to Prussian blue.[10] Of the other six-connected coordination polymers all are constructed by using more than one type of linkage between six-connected nodes[11] or, as is the case of the Cd^{II} compound formed with hexakis(imidazolylmethyl)benzene,[12] are perhaps better described as having a NaCl-like structure as it has two distinct six-connected nodes.

It has been demonstrated recently that 4,4′-bipyridine-*N,N*′-dioxide (L) can play the same important role as its genitor compound 4,4′-bipyridine in the construction of coordination polymers and, in contrast to 4,4′-bipyridine, with

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lanthanide ions.[14] Owing to the less sterically demanding nature of the pyridyl-*N*-oxide donor group, we report herein that L is particularly useful when constructing highly connected coordination frameworks such as those of the α-polonium-type or its related networks with early transition-metal centres.

It has also been demonstrated that the role of the counter-anion can be important when preparing coordination frameworks.[15] The anion can have two key effects upon the structure of the final product. Firstly, the co-ordinative ability of the anion can clearly influence the coordination sphere of the metal cation used and hence framework connectivity.[16] Secondly, the size of the anion can influence long-range order and degree of interpenetration if it is indeed present at all.[16] Thus, when designing coordination frameworks the role of the cation, counter-anion and ligand all need to be considered. In this study we report a series of related coordination frameworks using six-connected Sc^{III} nodes to generate the three-dimensional structure with 4,4′-bipyridine-*N*,*N*′-dioxide (L). We demonstrate that the size of the anion not only influences the degree of interpenetration but also the topology of the six-connected framework that is observed.

Results and Discussion

Reaction of $Sc(NO_3)_3$ or $Sc(CF_3SO_3)_3$ with $L{\cdot}xH_2O$ in MeOH or $MeOH/CH_2Cl_2$ affords **1** and **2**, respectively. In contrast, reaction of an aqueous solution of $Sc(ClO_4)_3$ with $L{\cdot}xH_2O$ in water, using different M:L ratios, afforded single crystals of **3** and **4**.

$\{[Sc(L)_3](NO_3)_3\}_\infty$ **1**

$\{[Sc(L)_3](CF_3SO_3)_3(CH_3OH)_{2.7}(H_2O)_3\}_\infty$ **2**

$\{[Sc(L)_3](ClO_4)_3\}_\infty$ **3**

$\{[Sc(L)_4(H_2O)_2](ClO_4)_3\}_\infty$ **4**

Single-crystal X-ray analysis of **1**–**3** confirms that these are polymeric structures based on networks of octahedrally co-ordinated ScO_6 centres bound through six oxygen atoms from six separate *N*-oxide ligands (Figure 1a–c). Although there are no previous examples of structurally characterised pyridine-*N*-oxide compounds of scandium, the Sc–O bond length of 2.074(2) Å in **1** and 2.083(6) Å (average) in **2** are comparable to those found for Sc^{III} complexes with carboxylates.[7] The Sc^{III} centre in **1** lies on a crystallographic $\bar{3}$ (S_6) centre with half a ligand in the asymmetric unit (Table 1).

Table 1. Selected bond lengths [Å] and angles [°] for **1**–**4**.

1		**2**		**3**		**4**	
Sc–O10	2.074(2)	Sc–O10	2.045(5)	Sc1–O1	2.079(2)	Sc1–O1	2.146(3)
		Sc–O20	2.066(5)			Sc1–O2	1.9750(5)
		Sc–O30	2.100(5)				
		Sc–O40	2.099(6)				
		Sc–O50	2.107(6)				
		Sc–O60	2.086(6)				
O10-Sc-O10^{i}	88.96(9)	O10-Sc-O20	175.6(2)	O1-Sc1-O1^{iv}	90.79(8)	O2-Sc1-O1	96.49(11)
O10-Sc-O10^{ii}	91.04(9)	O10-Sc-O30	86.0(2)			O1-Sc1-O1^{v}	90.73(3)
O10-Sc-O10^{iii}	180	O10-Sc-O40	88.0(2)			O1-Sc1-O1^{vi}	167.0(2)
		O10-Sc-O50	92.3(2)				
		O10-Sc-O60	91.7(2)				
		O20-Sc-O30	98.3(2)				
		O20-Sc-O40	92.8(2)				
		O20-Sc-O50	87.3(2)				
		O20-Sc-O60	84.0(2)				
		O30-Sc-O50	85.6(2)				
		O40-Sc-O30	89.9(2)				
		O40-Sc-O50	175.4(2)				
		O60-Sc-O40	90.8(2)				
		O60-Sc-O30	177.6(2)				
		O60-Sc-O50	93.8(2)				
N10-O10-Sc	131.5(2)	N10-O10-Sc	142.9(5)	N1-O1-Sc1	134.9(2)	N1-O1-Sc1	138.3(2)
		N20-O20-Sc	137.9(5)				
		N30-O30-Sc	123.5(4)				
		N40-O40-Sc	123.8(4)				
		N50-O50-Sc	119.1(4)				
		N60-O60-Sc	129.2(5)				

Symmetry transformations used to generate equivalent atoms: i: $x-y, x, -z$; ii: $-x+y, -x, z$; iii: $-x, -y, -z$; iv: $-y, x-y, z$; v: $1-y, x, -3-z$; vi: $1-x, 1-y, z$.

The extended structure shows that each ligand bridges adjacent Sc^{III} centres through its two oxygen atoms to form a rhombohedral array of α-polonium-type $4^{12}6^{3}$ topology with a Sc···Sc edge length of 12.8 Å and an acute inter-edge angle of 70.8° (Figure 2). Although the coordination environment at Sc^{III} in **1** is almost perfectly octahedral [O-Sc-O 88.96(9), 91.04(9), 180°], the Sc-O-N angle of 131.5(2)° adopted by the crystallographically planar 4,4′-pyridine-*N*,*N*′-dioxide ligand leads to a rhombohedral rather than cubic framework. The volume of this open rhombohedral box is 1628 $Å^3$, one third of the unit cell volume, allowing mutual interpenetration of two equivalent three-dimensional frameworks related by C_2 symmetry (Figure 2). The Sc nodes of one lattice lie at the body centre of the other resulting in a shortest inter-network Sc···Sc distance of 6.48 Å. The remaining unoccupied space between the two interpenetrating rhombohedral $\{[ScL_3]^{3+}\}_\infty$ networks is occupied by nitrate ions which sit in channels that run parallel to the crystallographic *c* axis (Figure 3).

In contrast to **1**, compound **2** crystallises in a monoclinic crystal system, and as in **1** the Sc^{III} cation adopts a homoleptic ScO_6 distorted octahedral coordination environment

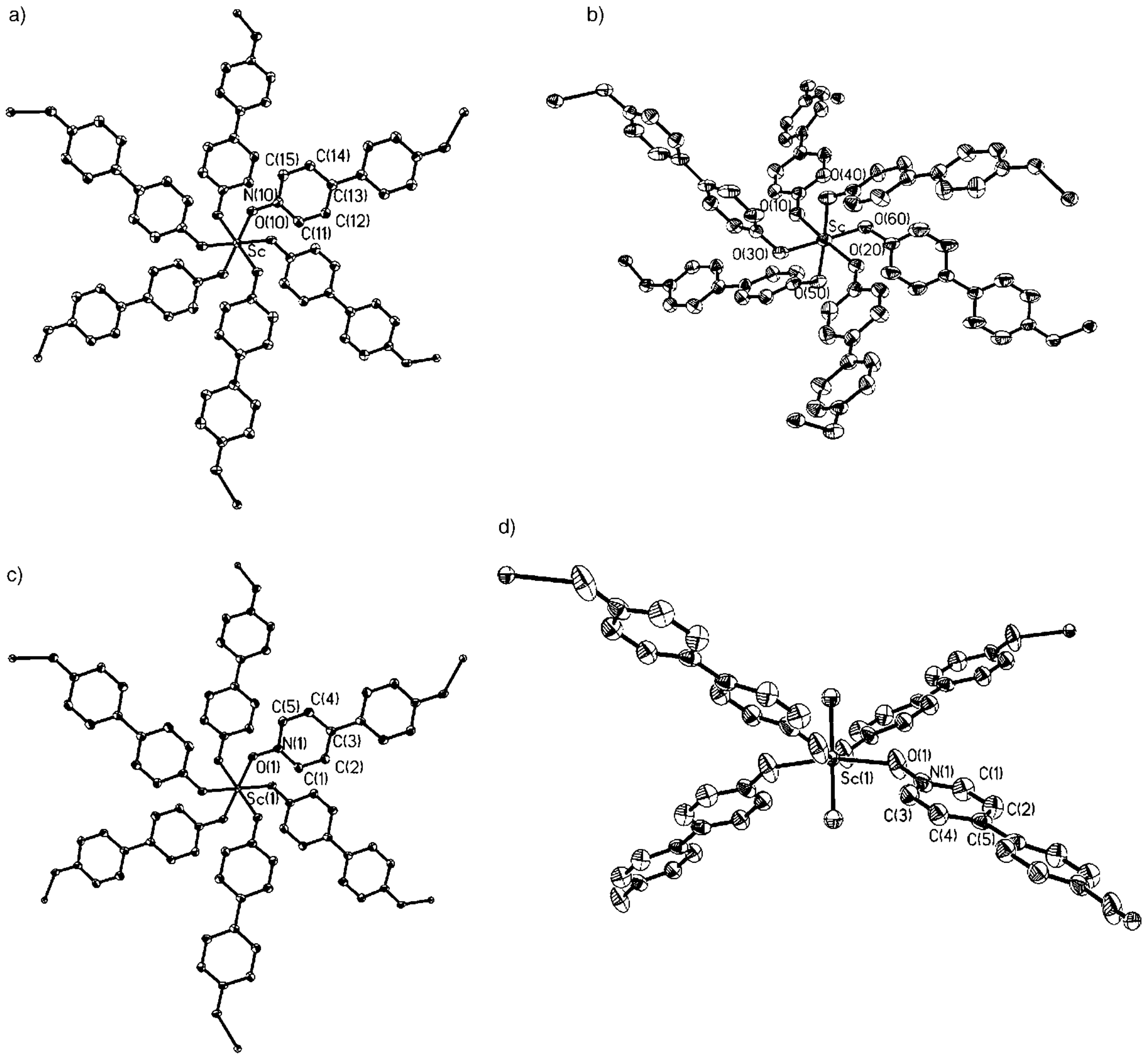

Figure 1. The coordination geometries at Sc^{III} in a) **1**, b) **2**, c) **3** and d) **4**. Hydrogen atoms are omitted for clarity.

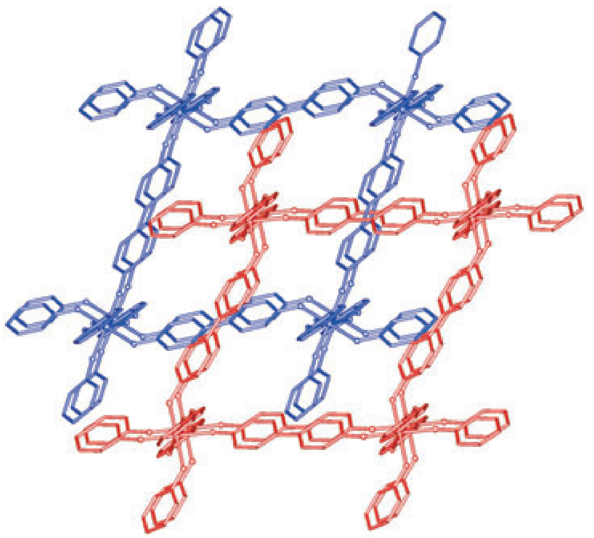

Figure 2. Two-fold interpenetrating networks of $\{[ScL_3]^{3+}\}_\infty$ in **1** (red and blue). Hydrogen atoms and anions are omitted for clarity.

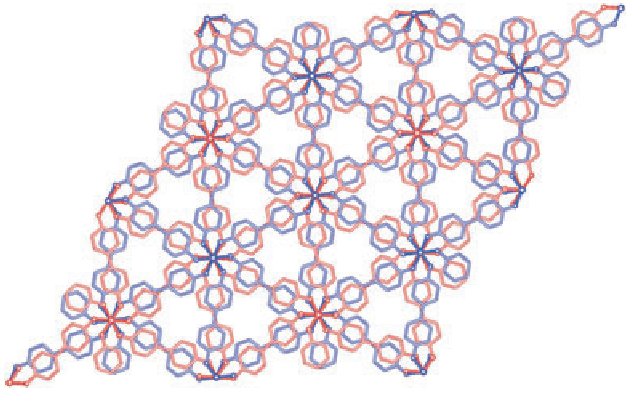

Figure 3. View of the channels formed in **1**. These run parallel to the crystallographic *c* axis and accommodate the NO_3^- ions. The two interpenetrating nets are represented in red and blue. Hydrogen atoms and anions omitted for clarity.

(Figure 1b; Table 1). Each Sc^{III} centre is bridged to six adjacent metal centres through 4,4′-bipyridine-*N*,*N*′-dioxide ligands to form a three-dimensional six-connected framework structure, with a wide range of Sc-O-N angles (119.1–142.9°) and intra-framework Sc···Sc distances (12.2 to 12.8 Å). Channels are formed within the cationic framework, which run parallel to the crystallographic *a* and *b* axes and host the $CF_3SO_3^-$ ions and guest MeOH and H_2O solvent molecules (Figure 4). The structural topology of **2** is 4^86^68 and is quite unusual (see below for a discussion of topological representations) in that a criss-crossed structure is observed which has displaced linkages between parallel (4,4) nets. This topology is quite distinct from the α-polonium structure, or other previously reported six-connected structures and, therefore, the cationic $\{[ScL_3]^{3+}\}_\infty$ networks observed in **1** and **2** are topological isomers.[17] Only one previous report of a related topology has been described[18] in $[Cd(CN)_2(pyrazine)]_\infty$, in which two kinds of linkages of CN^- and pyrazine were used. Thus, compound **2** serves as the first example of a homoleptic six-connected framework and cationic framework with this criss-cross motif.

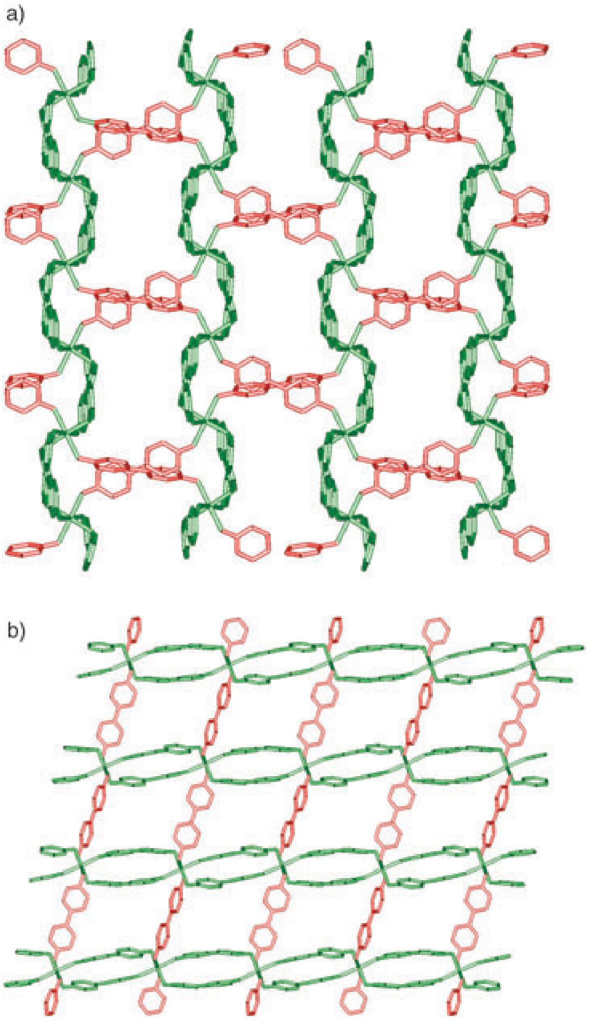

Figure 4. View of **2** parallel to the crystallographic *a* axis (a) and *b* axis (b) illustrating the channels which accommodate counter-anions and guest solvent molecules. (4,4) grids (green) are cross linked by further bridging ligands L (red) leading to a topological arrangement distinct to that observed in **1**. Hydrogen atoms, counter-anions and guest solvent molecules are omitted for clarity.

In contrast to the reactions of $Sc(NO_3)_3$ or $Sc(CF_3SO_3)_3$ with L in CH_3OH or CH_3OH/CH_2Cl_2, the reaction of $Sc(ClO_4)_3$ with L in water leads to the isolation of two distinct products, **3** and **4**. Compound **3** forms a structure that is highly related to that of compound **1**, a doubly interpenetrated six-connected three-dimensional array which crystallises in the same space group ($R\bar{3}c$). The geometric features of **3** are also similar to those observed in **1** (Table 1) but a slight increase is observed in the Sc···Sc edge length from 12.8 Å in **1** to 12.95 Å in **3** and an increase in the inter-network Sc···Sc distance from 6.48 Å in **1** to 7.91 Å in **3**. This allows an increase in the volume of the rhombohedral box within each cationic framework to 2061 $Å^3$ in **3** compared to 1628 $Å^3$ in **1**, which allows accommodation of the larger ClO_4^- counter-anions whilst maintaining framework interpenetration.

Compound **4** adopts an entirely different network structure whilst maintaining a six-coordinate Sc^{III} coordination environment and six-connected framework structure. Each Sc^{III} centre is coordinated by four molecules of L which serve as bridges to adjacent metal nodes. The octahedral coordination geometry at the metal centre is completed by two water molecules (Figure 1d) that act as bridges to adjacent metal centres thus generating a six-connected framework structure. Significantly, the bridges formed by L do not sit in a plane but a distorted tetrahedral geometry, and if these connections are considered alone (i.e. ignoring the water bridges) the resultant structure is a diamondoid array typically seen for tetrahedral connecting nodes (Figure 5). In this case the Sc-O-N angle of 138.3(2)° generated by the *N*-oxide moiety leads to the pseudo-tetrahedral geometry generated by the ScL_4 secondary building unit. Considering just the $[Sc(L)_2]_\infty$ frameworks then the structure exists as a fivefold interpenetrated diamondoid array, as have been observed previously for coordination framework structures of Cu^I with bipyridyl ligands.[5c] However, the bridging water molecules serve to bridge these diamondoid frameworks into a single three-dimensional array (Figure 5) of 4^86^7 topology (see below for a discussion of topological representations). Unusually, structural refinement of the X-ray structure of this compound reveals that the Sc atom is only half-occupied such that formally a vacancy exists at 50% of the networks nodes. This can readily accounted for by the adoption of a hydrogen-bonded node that utilises the presence of water molecules.[19] Such hydrogen-bond based nodes between coordinated water molecules and L have been observed previously[20] and represent a virtual six-connected topological node (as in previous examples). Thus, the Sc^{III} and hydrogen-bonding nodes are isotopological, allowing the formation of the uninodal 4^86^7 three-dimensional array to be considered. In subsequent discussions and descriptions **4** will be treated as a uninodal network.

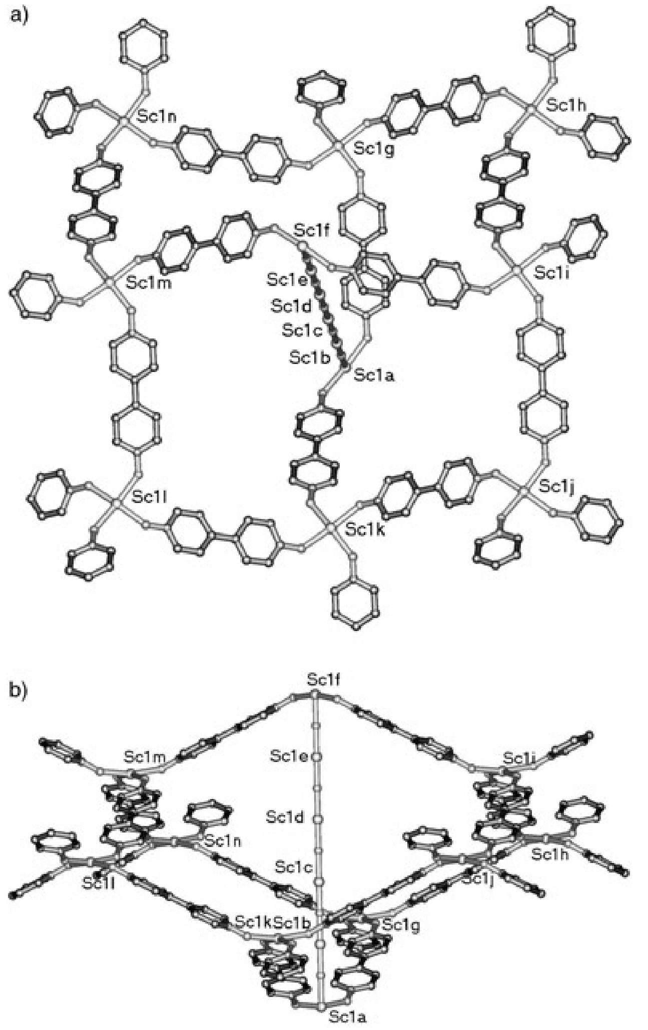

Figure 5. a,b) Views of **4** showing an adamantoid unit containing ten Sc^{III} ions bridged by molecules of L. The bridging of topological node [Sc^{III} ions or hydrogen-bonded nodes] by water molecules (Sc1a, Sc1b, Sc1c, Sc1d, Sc1e, Sc1f) is shown by the hollow line in (b). Sc1b–Sc1e represent metal centres that are constituent parts of four pseudo-interpenetrating diamondoid arrays.

Compounds **3** and **4** are prepared under different conditions from **1** and **2**, using an aqueous solution of the $Sc(ClO_4)_3$ starting material rather than methanolic solutions. The inclusion of water molecules within the structure of **4** is not surprising; indeed solvent inclusion is often encountered in coordination framework structures and can have a significant influence on the overall structure of the resultant product.[21]

Influence of anion: Assuming efficient close packing it can be deduced that by more than doubling the anionic volume on going from NO_3^-, or ClO_4^-, to $CF_3SO_3^-$[22] the possibility of adopting an identical doubly-interpenetrated α-polonium net in **1**, **2** and **3** is precluded. Thus, for **2** the space occupied by the $\{[ScL_3]^{3+}\}_\infty$ framework and the associated $CF_3SO_3^-$ ions corresponds to 65.1 % (3649 Å^3)[23] of the unit cell volume, representing greater than 50 % of the total volume, and thus precluding interpenetration. As no additional guest solvent molecules are included in the case of **1** or **3** it can be deduced that each framework, plus associated NO_3^- or ClO_4^- ions, occupies 50 % of the unit cell volume (2442 Å^3 in **1**, 2877 Å^3 in **3**) of which the anions occupy 15.7 % (767 Å^3) in **1** or 28.4 % (1631 Å^3) in **3**.[23]

As a direct structural analogue to **1** is ruled out by the use of the $CF_3SO_3^-$ ion, it can be concluded that no interpenetration will occur in **2** and a different space-filling mechanism must be adopted. As in the case of **2** and **4** the most common mechanism for space-filling which is adopted by three-dimensional frameworks, apart from interpenetration, is solvent inclusion. Owing to the highly variable and malleable nature of solvent assemblies it is possible for alternative structural arrangements to become favourable and thus new topologies can be encountered. This is the case for compounds **2** and **4**.

Topological representations: The structure of **1** and **3** of $4^{12}6^3$ topology can be described as comprising three intersecting (4,4) nets that share connections. This arrangement leads to layers of (4,4) nets cross-linked by co-linear connections to form a NaCl-type structure (Figure 6a). The structure of **2** can similarly be described in terms of cross-linked layers of (4,4) nets. However, in this case the links are not co-linear with alternating linkers adopting mutually inclined orientations whilst bridging adjacent (4,4) nets (Figure 6b). As a result of this changed orientation in the connections between (4,4) nets the topology of the material changes from $4^{12}6^3$ in **1** and **3** to $4^8 6^6 8$ in **2**. From the topological

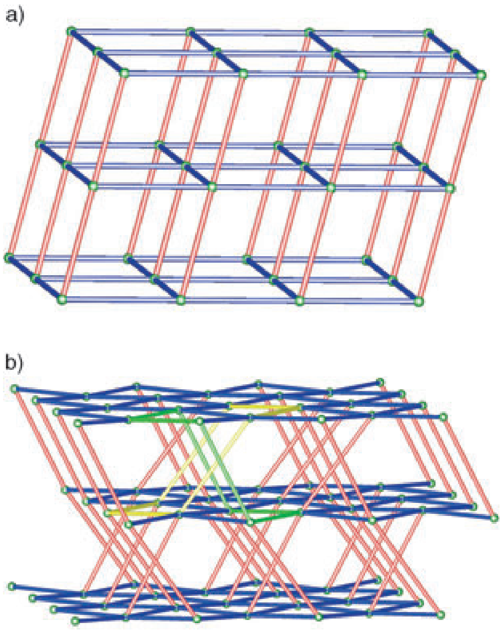

Figure 6. a) Topological representation of the structure of **1** and **3** leading to a $4^{12}6^3$ topology of the NaCl-type structure utilising co-linear connections between adjacent (4,4) nets. b) View of **2** showing the $4^8 6^6 8$ topology layers of (4,4) nets (blue), the linkers (red) and the self-penetrating shortest circuits (green and yellow).

symbol it can be seen that the number of four-membered circuits decreases in **2** where parallel, co-planar layers of (4,4) nets are observed (Figure 6b) rather than three intersecting (4,4) nets as observed in **1** and **3** (Figure 6a). The topology of **2** has been observed previously in [Cd(CN)$_2$(pyrazine)][18] and interestingly it represents an example of self-penetration. The six-membered shortest circuits involving connections between (4,4) nets are catenated by equivalent shortest circuits within the single network (Figure 6b).

The structure of **4** can be viewed as layers of (4,4) nets in two directions (as opposed to three directions for **1** and **3**, and one direction in **2**) comprising two ligands L and two bridging water molecules per circuit. However, connections in the third direction are divergent and do not form (4,4) nets. Thus, if the bridging ligands L are considered alone and the water molecules disregarded, from a topological perspective it can be seen that the divergent connections form a *pseudo-tetrahedral* Sc(L)$_4$ node resulting in a diamond-like structure that is itself fivefold interpenetrated. This interpenetrated structure is pillared by the water molecules resulting in the observed layers of (4,4) nets to afford an overall $4^8 6^7$ topology. As **4** can be viewed as five interpenetrated networks that are connected through the bridging water molecules, the resulting single network therefore exhibits self-penetration. The short Schläfli topological symbol can be derived by considering the four-membered shortest circuits that consist of two L ligands and two bridging water molecules and the six-membered circuits comprising only L ligands that form part of the diamond substructure. These six-membered shortest circuits are catenated by four other equivalent circuits, leading to a self-penetrating structure (Figure 7).

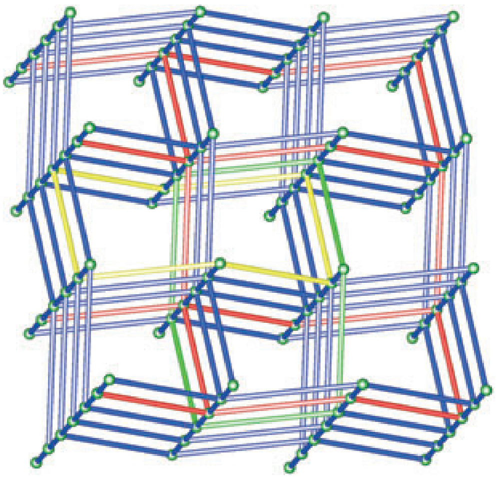

Figure 7. Representation of **4** showing a single diamondoid subnet (red) and the self-penetrating shortest circuits (green and yellow). The water molecules bridging topological nodes are orientated perpendicular to the page in this view.

Conclusion

The present structures represent new examples of organic/inorganic hybrid networks of six-connected structures. The isolation of compound **4** stresses the importance of reaction conditions upon network architectures and the significant influence that small changes in solvent can have. We have shown that by variation of anion size we are able to influence the degree of interpenetration and hence observed framework topology. Furthermore, the series of polymers reported herein illustrates how tectons based upon (4,4) grids can be combined and distorted to form non-NaCl topologies and even cross-bridged, multiply interpenetrated diamondoid materials. Thus α-polonium-type structures, of $4^{12}6^3$ topology, as observed in **1** and **3**, mimic the expected six-connected NaCl structure albeit with the additional feature of double-interpenetration. Alternate non-NaCl structures can also be generated incorporating either criss-crossed connected co-planar layers of (4,4) nets in a unique $4^8 6^6 8$ topology, or a diamondoid array based upon a tetrahedral node with bridging water molecules serving to bridge these diamondoid frameworks into a single, self-penetrating, three-dimensional array of $4^8 6^7$ topology. Thus, framework polymer materials represent powerful systems for investigating and defining new solid-state structures and topologies.

Whereas the vast majority of coordination polymers have been prepared using the later transition metals, particularly those of Groups 11 and 12, the use of bis(pyridyl-*N*-oxide) ligands in constructing coordination polymers also offers great potential for exploiting the *earlier* transition metals. We believe that this will lead to both the design and discovery of a large variety of new network structures and types.

Experimental Section

Sc(NO$_3$)$_3$, aqueous solution of Sc(ClO$_4$)$_3$ and 4,4′-bipyridine-*N*,*N*′-dioxide hydrate were used as received (Aldrich) without further purification. Infra-red spectra were recorded on a Perkin-Elmer 1600 spectrometer (FTIR, samples in KBr discs). Elemental analyses were performed by the Nottingham School of Chemistry microanalytical service.

Synthesis

{[Sc(L)$_3$](NO$_3$)$_3$}$_\infty$ (1): 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (66 mg, 0.30 mmol) in MeOH (15 mL) was carefully mixed with a solution of Sc(NO$_3$)$_3$·xH$_2$O (34 mg, 0.10 mmol) in MeOH (10 mL). The reaction gave a colourless crystalline product after 10 days. Yield 45 mg (56%). Comparison of the single-crystal data with that from powder X-ray diffraction studies of bulk samples confirmed that a single phase of **1** is isolated from the above reaction. Elemental analysis calcd (%) for $C_{30}H_{24}N_9O_{15}Sc$: C 45.29, H 3.04, N 15.85; found: C 43.42, H 3.18, N 15.70.

{[Sc(L)$_3$](CF$_3$SO$_3$)$_3$(CH$_3$OH)$_{2.7}$(H$_2$O)$_3$}$_\infty$ (2): 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (22 mg, 0.10 mmol) in methanol (5 mL) and Sc(CF$_3$SO$_3$)$_3$ (15 mg, 0.03 mmol) in MeOH (5 mL) were individually added to the two branches of a U-tube, which already contained a CH$_2$Cl$_2$ (3 mL) buffer in its central segment. The reaction gave a colourless crystalline product after 20 days. Yield 7 mg (20%). Elemental analysis calcd (%) for $C_{35.7}H_{40.8}F_9N_6O_{20.7}S_3Sc$: C 35.81, H 3.43, N 7.02; found: C 34.80, H 2.61, N 7.58.

{[Sc(L)$_3$](ClO$_4$)$_3$}$_\infty$ (3): 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (20 mg, 0.1 mmol) in H$_2$O (5 mL) was carefully mixed with a solution of

Table 2. Summary of crystallographic data for **1**–**4**.

	1	**2**	**3**	**4**
chemical formula	$C_{30}H_{24}N_9O_{15}Sc$	$C_{35.7}H_{40.8}F_9N_6O_{20.7}S_3Sc$	$C_{30}H_{24}Cl_3N_6O_{18}Sc$	$C_{40}H_{36}Cl_3N_8O_{22}Sc$
M_r	795.54	1197.28	907.86	1132.08
crystal system	trigonal	monoclinic	trigonal	tetragonal
space group	$R\bar{3}c$	$P2_1/n$	$R\bar{3}c$	$I\bar{4}2d$
a [Å]	20.852(3)	20.7872(7)	20.4951(14)	23.995(4)
b [Å]	–	12.8061(6)	–	–
c [Å]	12.972(2)	21.6247(12)	15.818(2)	3.9498(9)
α [°]	90	90	90	90
β [°]	90	103.246(3)	90	90
γ [°]	120	90	120	90
V [Å^3]	4884.6(12)	5603.4(4)	5754.1(9)	2274.1(7)
Z	6	4	6	2
T [K]	150(2)	120(2)	150(2)	150(2)
μ [mm^{-1}]	0.317	0.346	0.486	0.435
reflections collected	6862	64157	11331	4386
unique reflections (R_{int})	1251 (0.099)	10368 (0.256)	1467 (0.048)	1415 (0.076)
final R_1 [$F > 4\sigma(F)$]	0.058	0.118	0.0464	0.0726
wR_2 (all data)	0.129	0.294	0.146	0.223

$Sc(ClO_4)_3$ (12 mg, 0.03 mmol; 40 wt% in H_2O) and the solution was allowed to evaporate slowly. The reaction yielded a colourless crystalline product after 10 days.

$\{[Sc(L)_4(H_2O)_2](ClO_4)_3\}_\infty$ (4): 4,4′-Bipyridine-*N*,*N*′-dioxide hydrate (10 mg, 0.05 mmol) in H_2O (5 mL) was carefully mixed with a solution of $Sc(ClO_4)_3$ (15 mg, 0.05 mmol; 40 wt% in H_2O) and the solution was allowed to evaporate slowly. The reaction yielded a colourless crystalline product after 14 days.

X-ray data collection, solution and refinement: Crystal data and summaries of the crystallographic analyses for all complexes are given in Table 2. Diffraction data for compounds **1** and **2** were collected on a Nonius Kappa CCD area detector diffractometer, equipped with an Oxford Cryosystems open flow cryostat[24] and controlled by the Collect software package. Collected images were processed by using Denzo.[25] The data were corrected for absorption by using the empirical method employed in Sortav.[26] Diffraction data for compound **3** was collected on a Bruker SMART 1000 CCD area detector and compound **4** a Bruker SMART APEX CCD area detector equipped with an Oxford Cryosystems open flow cryostat.[24] The collected images were processed by using SAINT and SHELXTL-97. All four structures were solved by direct methods using SHELXS-97[27] and full-matrix least squares refinement was undertaken using SHELXL-97.[28] All hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **2** all guest methanol and water molecules were refined with partial occupancies, with C–O distances restrained to 1.42 Å. No hydrogen atoms were either located or placed on any of the abovementioned disordered methanol or water molecules. The high values for R_1 and R_{int} reflect the small and weakly diffracting crystal that the data were collected on and that the structure contains a considerable amount of disordered solvent.

CCDC-241335 (**1**), CCDC-241336 (**2**), CCDC-241337 (**3**), and CCDC-241338 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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