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Stereoisomeric Doubly Interpenetrating Three-Dimensional Networks of Tripodal Neodymium(III) Complexes from Spacer-Controlled Enantioselective Self-Assembly

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Two three-dimensional frameworks composed of doubly interpenetrating networks of the same topology but different stereoisomeric structures have been constructed from self-assembly of the chiral building block, Δ- or Λ-$[\mathrm{Nd(ntb)_2}]^{3+}$, with different spacers bipy and bpen (ntb = tris(2-benzimidazolylmethyl) amine, bipy = 4,4′-bipyridyl, bpen = *trans*-1,2-bis (4-pyridyl)ethylene). In the crystal structure of $[\mathrm{Nd(ntb)_2}](\mathrm{ClO_4})_3\cdot3\mathrm{bipy}\cdot2\mathrm{H_2O}$ the spacer bipy connects $[\mathrm{Nd(ntb)_2}]^{3+}$ cations of the same handedness to generate a chiral network Δ_3-Δ…(or Λ_3-Λ…)$\{[\mathrm{Nd(ntb)_2}](\mathrm{bipy})_3\}^{3+}{}_{\infty}$, which is interpenetrated further by another identical network. The crystal structure of $[\mathrm{Nd(ntb)_2}](\mathrm{ClO_4})_3\cdot3\mathrm{bpen}\cdot\mathrm{H_2O}$ shows a topologically similar but achiral framework in which non-planar and planar bpen spacers connect cations of the same chirality and a pair of enantiomers, respectively, thus generating a three-dimensional racemate $\Delta_2\Lambda$-Λ…(or $\Lambda_2\Delta$-Δ…)$\{[\mathrm{Nd(ntb)_2}](\mathrm{bpen})_3\}^{3+}{}_{\infty}$. Aggregation of the molecular species is effected by N-H···N hydrogen bonds, and the observed enantioselective self-assembly can be rationalized by π···π interactions between aromatic rings.

Keywords: Tripodal ligand, neodymium(III) complex, spacer, framework, self-assembly, chirality

INTRODUCTION

The crystal engineering of supramolecular arrays is currently one of the most important areas of research that has implications for the rational design of functional materials.[1] Two major directions[2] have been actively pursued: the construction of organic networks consolidated by directional non-covalent interactions,[3] and that of coordination polymers sustained by coordinate covalent bonds.[4] More recently, design strategies relying on the incorporation of both types of interactions have become increasingly prominent. This fascinating approach is dominated by supramolecular self-assembly, which is natural in origin and presently generally harnessed in unnatural systems.[5] The self-assembly of chiral supramolecular entities is common *in vivo*. However, the design of artificial chiral self-assembling systems with coordination

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motifs is regarded as a new endeavor and therefore quite challenging.[6] Lehn and co-workers[7] have proposed that supramolecular chirality may be achieved if (i) at least one component is asymmetric, or (ii) the interaction between achiral components is dissymmetrizing, yielding a chiral association. Based on the second principle, various helical arrays[8] and chiral frameworks[9]have been synthesized. On the other hand, self-assembly using chiral coordination motifs that are held together by non-covalent interactions is less explored, although some self-assemblies of diverse chiral molecular squares have been reported.[6,10] In a previous paper,[11] we reported doubly interpenetrating two- and three-dimensional networks, with an encapsulated lanthanide(III) cation $[Ln(ntb)_2]^{3+}$ **1** as the building block and hydrogen-bonded 4,4'-bipyridyl as a spacer, in three related complexes $[Pr(ntb)_2](ClO_4)_3 \cdot 2bipy \cdot 1.5H_2O$ **2** and $[Ln(ntb)_2](ClO_4)_3 \cdot 3bipy \cdot nH_2O$ (**3**, Ln = Eu, $n = 2$; **4**, Ln = Tb, $n = 1$). Here we describe the construction of stereoisomeric doubly interpenetrating three-dimensional networks in $[Nd(ntb)_2](ClO_4)_3 \cdot 3bipy \cdot 2H_2O$ **5** and $[Nd(ntb)_2](ClO_4)_3 \cdot 3bpen \cdot H_2O$ **6** from enantioselective self-assembly of the same $[Nd(ntb)_2]^{3+}$ building block with the spacers bipy and bpen (bipy = 4,4'-bipyridyl, bpen = *trans*-1,2-bis(4-pyridyl)ethylene), placing particular emphasis on the stereochemical diversity resulting from the size and conformational preference of different spacers.

RESULTS AND DISCUSSION

The tripodal ligand tris(2-benzimidazolylmethyl)amine (ntb) reacts with hydrated lanthanide(III) nitrates to give 1:1 complexes $[Ln(ntb)(NO_3)_3] \cdot H_2O$,[12] while with perchlorate salts a 2:1 $[Ln(ntb)_2]^{3+}$ cation[11,13] is formed, which can be readily assembled by spacer 4,4'-bipyridyl to produce hydrogen-bonded networks.[11] The present pair of complexes were synthesized using the same neodymium(III) ion but different spacers bipy and bpen, and were characterized by single crystal X-ray analysis. Information concerning crystallographic data and structure refinement is given in Table I.

In both $[Nd(ntb)_2](ClO_4)_3 \cdot 3bipy \cdot 2H_2O$ **5** and $[Nd(ntb)_2](ClO_4)_3 \cdot 3bpen \cdot H_2O$ **6**, each ntb ligand displays a tripod-like tetradentate coordination mode with the metal ion surrounded by six benzimidazole arms of two ntb ligands to give a $[Nd(ntb)_2]^{3+}$ sepcies. Thus the central Nd(III) ion is eight coordinated and encapsulated in a slightly distorted cubic environment.[11,13]The Nd-N bond distances show no remarkable features and closely resemble each other in **5**and **6**, and selected bond distances and bond angles are listed in Table II. Since the $[Nd(ntb)_2]^{3+}$ cations in **5** and **6** are isostructural, only the molecular structure and atomic numbering scheme for **5** are depicted in Fig. 1. The pair of tripodal ntb ligands wrap around the Nd^{3+} ion in such a way that a C_3 axis (*pseudo*-C_3 in **6**) passes through the two apical tertiary amino nitrogen atoms and the central metal atom. Viewing down this C_3axis from either apical nitrogen atom to the Nd^{3+} ion in opposite directions, the two ntb ligands have the same right- or left-handed propeller appearance. This type of helical arrangement is intrinsically chiral and results in a pair of enantiomers. The Δ and Λ enantiomers of $[Nd(ntb)_2]^{3+}$ are defined as shown in Scheme 1. Viewing down the C_3axis along a N-M bond, if the arms of the top ntb ligand wrap around the central metal ion in a clockwise propeller-like fashion, the chirality symbol Δ is assigned; conversely, if the propeller takes an anti-clockwise shape, the symbol Λ is applicable.[14] The ntb ligand itself is achiral in solution, so that its chelation to the Nd(III) ion is expected to produce enantiomeric $[Nd(ntb)_2]^{3+}$ cations in equal numbers. As each ntb ligand possesses three NH groups that are potential hydrogen-bond donors (see Fig. 2), it is possible in principle to self-assemble the $[Nd(ntb)_2]^{3+}$ motifs by employing a linear difunctional hydrogen-bond acceptor such as bipy or bpen as a spacer component, and the stereochemistry of the resulting supramolecular array may be profoundly affected by the spacer used.

TABLE I Data collection and processing parameters of **5** and **6**

Complex	**5**	**6**
Empirical formula	$C_{78}H_{70}Cl_3N_{20}NdO_{14}$	$C_{84}H_{74}Cl_3N_{20}NdO_{13}$
Color and habit	pale purple prism	pale purple prism
Crystal size (mm)	0.3 × 0.3 × 0.2	0.4 × 0.36 × 0.3
Crystal system	rhombohedral	monoclinic
Space group	*R*32 (No. 155)	*C*2/*c* (No. 15)
Unit cell dimensions		
a (Å)	16.403(2)	22.147(4)
b (Å)	16.403(2)	16.082(3)
c (Å)	27.497(5)	26.748(5)
α(deg.)	60	90
β(deg.)	60	113.66(3)
γ(deg.)	120	90
Volume ($Å^3$)	6407(2)	8726(3)
Z	3	4
Formula weight	1762.13	1822.22
Density (cal.) (Mg/m^3)	1.370	1.387
Absorption coefficient (mm^{-1})	0.774	0.759
F(000)	2703	3732
Temperature (K)	293(2)	293(2)
Theta range (deg)	1.61 to 23.26	1.62 to 25.63
Reflections measured	7875	13150
Index ranges of measured data	*h*, –18 – 15; *k*, –15 – 17; *l*, –30 – 19	*h*, –26 – 0, *k*, –19 –19; *l*, –29 – 31
Independent reflections	2064 (Rint = 0.0703)	7554 (Rint = 0.0729)
Observed reflection	2048 ($I > 2\sigma(I)$)	6895 ($I > 2\sigma(I)$)
Absorption correction	None	ABSCOR
Relative transmission factors		0.815 – 1.139
Number of variables	174	537
Final *R* indices (obs.)	$R1 = 0.047$	$R1 = 0.083$
R indices (all)	$wR2 = 0.123$ $R1 = 0.052$	$wR2 = 0.233$ $R1 = 0.088$
	$wR2 = 0.146$	$wR2 = 0.240$
Goodness-of-fit index	1.06	1.11
Largest and mean Δ/σ	0.006, 0.001	0.031, 0.005
Largest difference peak ($eÅ^{-3}$)	0.731, –0.478	0.832, –0.610

TABLE II Selected bond lengths (Å) and angles (deg)

(i) Complex **5**			
Nd(1)-N(1)	2.776(3)	Nd(1)-N(3)	2.573(2)
N(3)-Nd(1)-N(1)	63.10(4)	N(3)#2-Nd(1)-N(1)	116.90(4)
N(3)#1-Nd(1)-N(3)	101.12(5)	N(3)#2-Nd(1)-N(3)	175.0(2)
N(3)#3-Nd(1)-N(3)	82.9(2)	N(3)#4 Nd(1)-N(3)	75.1(2)
Hydrogen bonding			
N(2)···N(4)#3	2.832	N(2)-H(2a)···N(4)#3	165.3
Symmetry transformations used to generate equivalent atoms:			
#1 -*x*+*y*+2, -*x*+2, *z* #3 *y*+2/3, *x*-2/3, -*z*+4/3		#2 *x*-*y*+2/3, -*y*+4/3, -*z*+4/3 #4 -*x*+8/3, -*x*+*y*+4/3, -*z*+4/3	
(ii) Complex **6**			
Nd(1)-N(1)	2.768(3)	Nd(1)-N(21)	2.536(4)
Nd(1)-N(11)	2.544(4)	Nd(1)-N(31)	2.550(4)
N(1)#1-Nd(1)-N(1)	178.52(15)	N(11)-Nd(1)-N(1)	63.74(11)
N(21)-Nd(1)-N(1)	63.89(11)	N(31)-Nd(1)-N(1)	63.98(11)
N(11)#1-Nd(1)-N(1)	116.20(11)	N(21)#1-Nd(1)-N(1)	114.84(11)
N(31)#1-Nd(1)-N(1)	117.34(11)	N(21)-Nd(1)-N(11)	101.88(12)
N(21)-Nd(1)-N(31)	103.04(12)	N(11)-Nd(1)-N(31)	101.27(13)
N(21)#1-Nd(1)-N(11)	75.16(12)	N(21)-Nd(1)-N(21)#1	79.13(16)
N(11)#1-Nd(1)-N(11)	176.27(17)	N(31)#1-Nd(1)-N(31)	74.96(16)
N(21)-Nd(1)-N(31)#1	176.21(13)	N(11)-Nd(1)-N(31)#1	81.74(13)
Hydrogen bonding			
N(12)···N(2)#2	2.775	N(12)-H(12a)···N(2)#2	169.5
N(22)···N(3)#3	2.730	N(22)-H(22a)···N(3)#3	170.5
N(32)···N(4)#4	2.838	N(32)-H(32a)···N(4)#4	167.9
Symmetry transformations used to generate equivalent atoms:			
# 1 -*x*+1, *y*, -*z*+1/2 #3 -*x*+3/2, -*y*+1/2, -*z*+1		#2 *x*+1/2, *y*+1/2, *z* #4 *x*, -*y*, *z*-1/2	

Single crystal X-ray analysis has shown that in both **5** and **6** the $[Nd(ntb)_2]^{3+}$ building block is involved in six donor hydrogen bonds with six neighbouring bipy or bpen units. The supramolecular hydrogen-bonding scheme is represented in Fig. 3. There is only one crystallographically unique N-H···N hydrogen bond in **5** (N(2)···N(4b), 2.832 Å, N(2)-H(2a)···N(4b), 165.3°), while in **6** six N-H···N hydrogen bonds are generated by the two-fold axis through the central Nd(III) ion from three independent ones (N···N, 2.774–2.838 Å; N-H···N, 167.5–170.5°; see Table II). Alternate linkage between a single $[Nd(ntb)_2]^{3+}$ motif with three different adjacent bipy or bpen molecules leads to an open three-dimensional cationic network (Fig 4a) with large voids to be filled by another identical interlocking network (Fig. 4b). The resulting

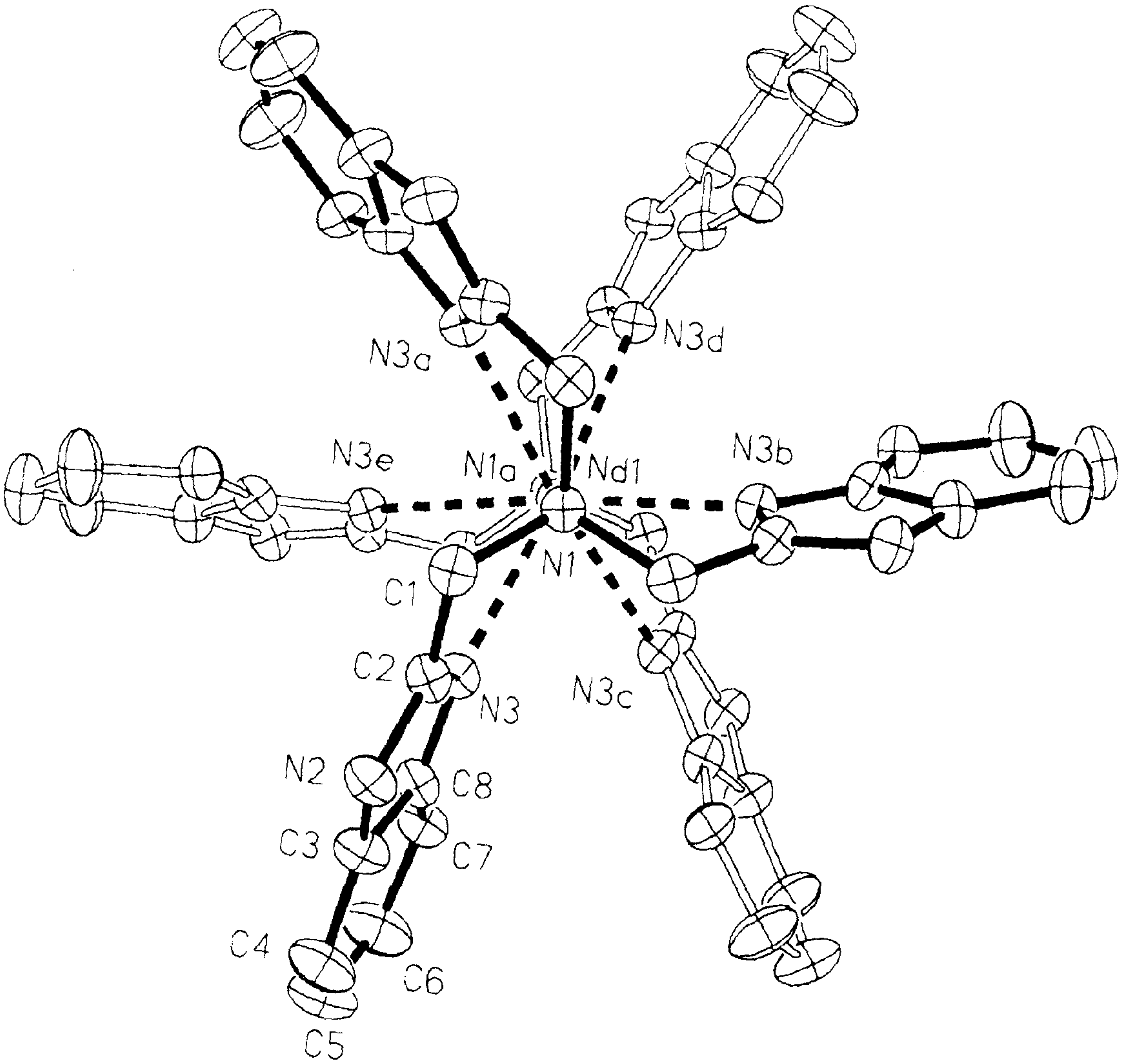


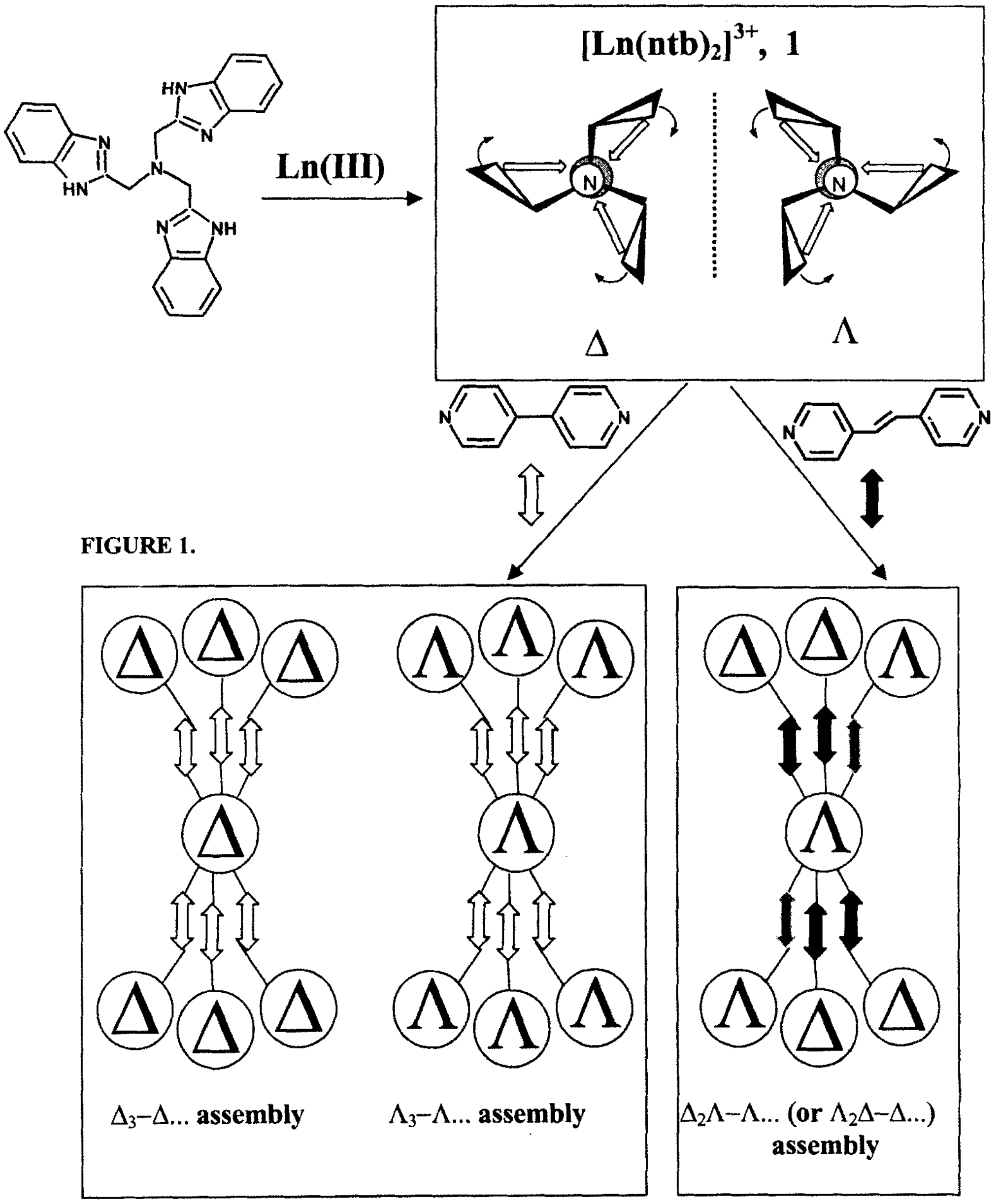
FIGURE 1 Top view of the cation [Nd(ntb)$_2$]$^{3-}$ (Λ configuation) in complex 5 showing atoms as thermal ellipsoids at 30% probability level. All H atoms have been omitted for clarity

three-dimensional framework of **5** (Fig. 5) is essentially the same as those of **3** and **4**, but exists in a space group of higher symmetry, suggesting that crystal symmetry increases with the ionic radius of the metal center. The network of both **5** and **6** may be assigned to the α-polonium-related topology as shown in Fig. 6.[15] The main difference is that larger voids are formed in **6**. As illustrated in Fig. 6, the separation between neighboring metal atoms within an independent network is *ca.* 20.6 Å in **5**, and 21.5–23.1 Å in **6**. The closest distance between metal atoms belonging to two interlocking networks is *ca.* 13.2 Å in **5**, and 13.7 Å in **6**. This difference between **5** and **6** is obviously associated with the structural characteristics of the spacers used: the distance between the terminal nitrogen atoms in bipy is 7.0 Å, while that in bpen is 9.4 Å. Obviously, the longer spacer bpen only results in a looser interlocking of the two networks but does not change the network topology.

The most striking feature of the three-dimensional frameworks of **5** and **6** is that their stereochemistry is controlled by the spacer employed. In **5**, the spacer bipy promotes aggregation of isomers of the same chirality to give an extended three-dimensional network designated as Δ_3-Δ... or Λ_3-Λ.... Two such networks of the same handedness interpenetrate each other to form a chiral framework. On the other hand, the non-planar and planar bpen spacers in **6** connect the same chiral $[Nd(ntb)_2]^{3+}$building blocks and a pair of enantiomers, respectively, thereby generating a three-dimensional racemic compound[14] $\Delta_2\Lambda$-Λ... (or $\Lambda_2\Delta$-Δ...) of the same network topology as **5**. Since the ligand ntb is achiral in solution, and coordination of ntb to Ln^{3+}produces a racemic mixture of enantiomeric Δ and Λ building blocks, the hydrogen-bonding driven self-assembly process may be considered to be enantioselectively spacer-controlled as illustrated in Scheme 1.

The intrinsic reason that causes this stereochemical diversity may be found from the π-π aromatic interactions between the spacers and the benzimidazole rings of the ntb ligands, because the same building blocks and the similar lattice architecture shared by **5** and **6** can provide insights into the observed stereochemical difference. In general, the spacers bipy and bpen are both linear difunctional and composed of two pyridyl rings. However, the single bond between the pyridyl rings in bipy can rotate freely, while rigidity of the ethylene double bond in bpen favors the coplanar conformation. The crystal structure analysis shows that the two six-numbered rings of bipy in **5** make a dihedral angle of *ca* 31°, which seems to be a favorable conformation of bipy for connecting a pair of neighbouring $[Nd(ntb)_2]^{3+}$ motifs of the same chirality. As shown in Fig. 7a, each bipy forms two face-to-face aromatic interactions with two adjacent benzimidazole rings of one $[Nd(ntb)_2]^{3+}$ motif, the centroid-to-centroid distance (d) and corresponding interplanar angle (τ) being 4.65 Å and 21°, respectively, plus two edge-to-face interactions with two adjacent benzimidazole rings of another $[Nd(ntb)_2]^{3+}$ motif at $d = 5.35$ Å and $\tau = 44.5°$.[16] Thus two $[Nd(ntb)_2]^{3+}$ motifs separated by one bipy exhibit the same chirality. Each $[Nd(ntb)_2]^{3+}$ motif in the *a,b* plane is positioned at the center of a hexagon composed of six surrounding $[Nd(ntb)_2]^{3+}$ motifs. As shown in Fig. 7b, adjacent motifs are separated by a bipy ligand, and the six bipy ligands surrounding a central motif are involved in twelve face-to-face and twelve edge-to-face aromatic interactions between the central and the neighboring motifs, all of which having the same chirality. On the other hand, the bpen ligand in **6** takes two kinds of conformation: in one its six-numbered rings are nearly coplanar and in the other they make a dihedral angle of 36.2°. The latter "torsional" one separates two $[Nd(ntb)_2]^{3+}$ motifs of the same handedness, as in the case of bipy in **5**, but the former "coplanar" one serves as a bridge between a pair of enantiomeric $[Nd(ntb)_2]^{3+}$ motifs. This relationship can be dipicted in Fig. 8a, in which the torsional bpen forms two face-to-face aromatic interactions with two adjacent benzimidazole rings of one $[Nd(ntb)_2]^{3+}$ motif at $d=$ 4.58 Å and $\tau = 17.4°$, and two edge-to-face interactions with two adjacent benzimidazole rings of another $[Nd(ntb)_2]^{3+}$ motif at $d = 5.06$ Å and $\tau = 48°$. On the contrary, each of the two independent coplanar bpen spacers is nearly parallel to two benzimidazole rings of a pair of neighbouring enantiomeric $[Nd(ntb)_2]^{3+}$ motifs and perpendicular to two adjacent benzimidazole rings of them (Fig. 8a), thus showing two face-to-face π-π interactions (d lie in the range of 3.77–4.37 Å and τ in the range of 7.3–8.6°) and two edge-to-face interactions (d, 4.62–5.03 Å; τ, 56–76.4°). A racemic layer matching the (200) plane may be best described as composed of rows of $[Nd(ntb)_2]^{3+}$ enantiomers in an alter-

Scheme 1.



SCHEME 1

nate arrangement along the *c* axis (Fig. 8b). Within each row running parallel to the *b* axis, adjacent motifs of the same chirality are separated by a torsional bpen ligand, and between adjacent rows the enantiomeric motifs are separated by coplanar bpen ligands.

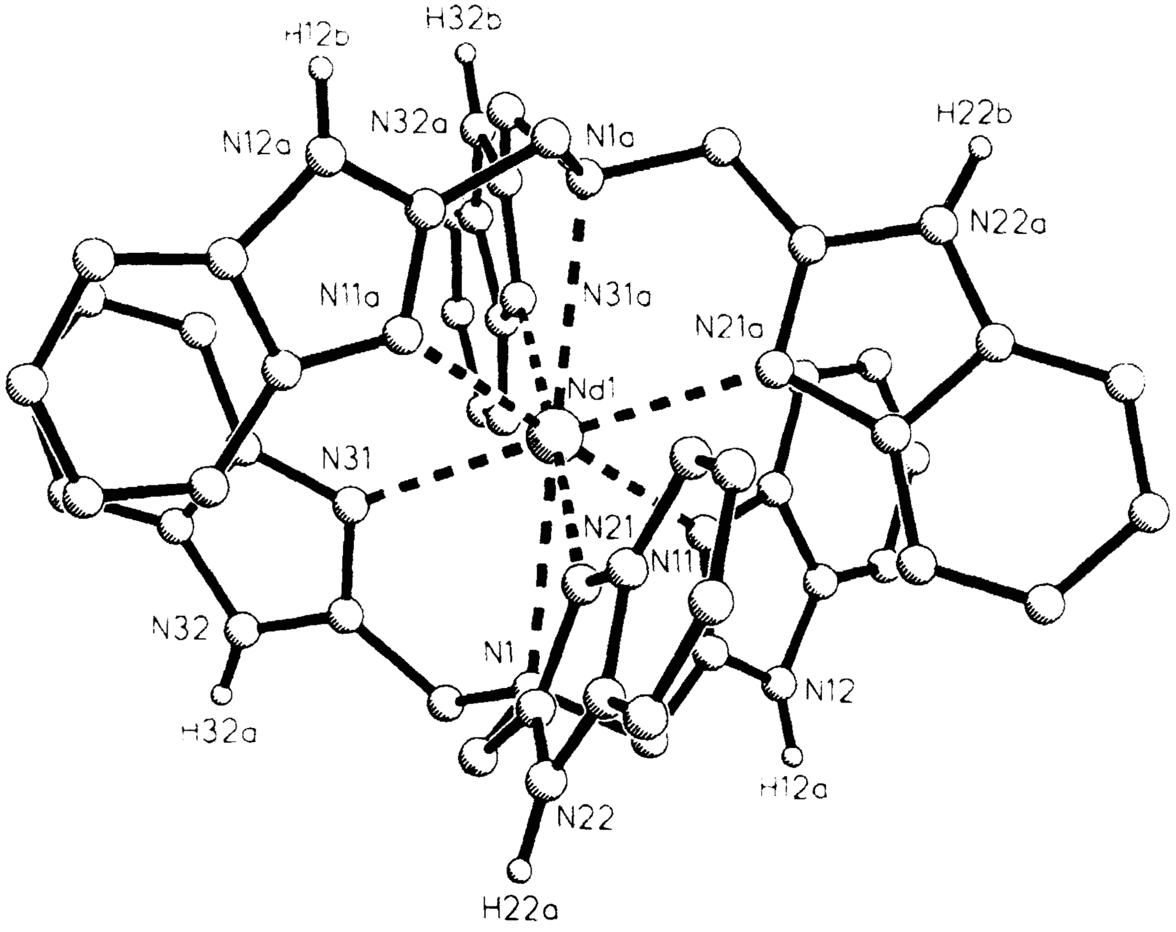


FIGURE 2 Side view of the cation $[Nd(ntb)_2]^{3+}$ in complex **6**. Note that the six NH groups that point in opposite directions are potential hydrogen-bond donors

From the above discussion we can see that the clustering of π-π interactions play an important role in stabilizing the supramolecular assembly of $[Nd(ntb)_2]^{3+}$ building blocks with bipy or bpen.[17] Especially in **6** the stabilization energy is strong enough to compensate for the destruction of the conformation energy of bpen. Most importantly, this stabilization makes it practicable to control the stereoselectivity of self-assembly by hydrogen bonding. The crystal structure analysis results demonstrate that the stereochemical structure of the three-dimensional frameworks is closely related to the conformation of the spacers. In other words, stereochemical recognition between the spacers and the building blocks can determine the chirality of the resulting frameworks. From Fig. 4 and 5 we can see that the networks may be considered to be constructed from the hydrogen-bonding self-assembly of layers of $[Nd(ntb)_2]^{3+}$ building blocks with bipy or bpen spacers. In addition, a torsional spacer excludes either inversion or mirror symmetry so that it connects the same chiral building blocks, whereas a coplanar spacer is compatible with

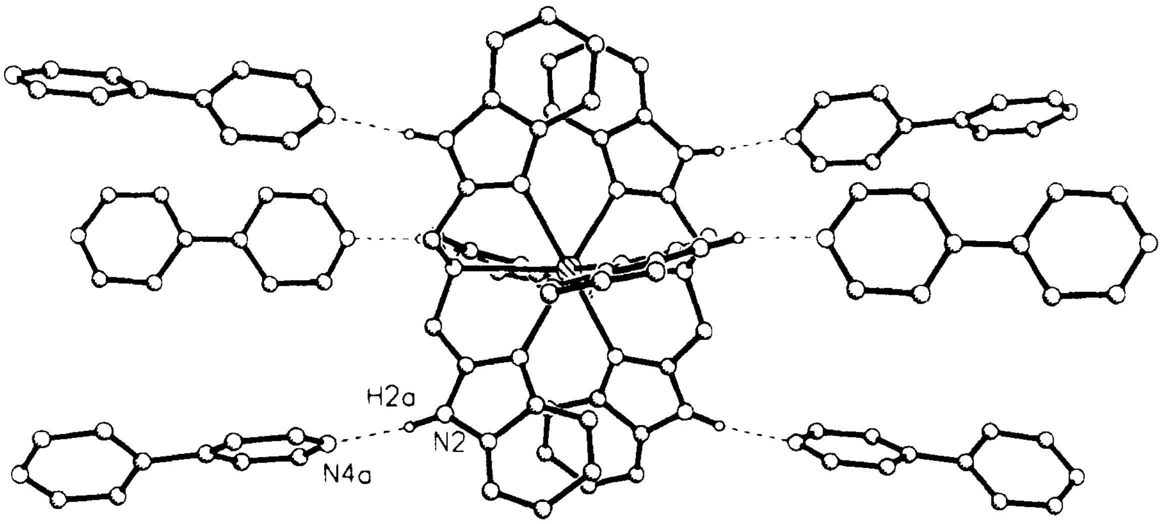


FIGURE 3 The supramolecular hydrogen-bond scheme in complex **5** showing that each $[Nd(ntb)_2]^{3-}$ motif forms six donor hydrogen-bonds with six neighboring bipy spacers

inversion symmetry and a pair of enantiomers can be bridged, as illustrated in Scheme 1. This enantioselective assembly necessitates that the layers assembled by bipy in **5** have the same chirality, and a chiral network is formed accordingly. Since each layer is interpenetrated by the bipy spacers of another network, both interlocking networks must also have the same chirality. On the other hand, in **6** the coplanar bpen joins a pair of enantiomeric building blocks while the torsional bpen connects building blocks of the same chirality, so the racemic layers assembled by both coplanar and torsional bpen result in a racemic network which is interlocked by an identical one.

The network of **6** represents another type of crystalline racemate that is different from the known examples[9d,9e] in which equivalent networks of opposite handedness interpenetrate each other. On the other hand, spontaneous resolution has been found in the assembly of metallohelical compexes[17b,18] involving both hydrogen bonding and coordinate bonding. However, to our knowledge most of the reported chiral networks[9a-c,15] are coordination polymers, and chirality is often achieved based on the second principle proposed by Lehn and co-workers.[7] Since achiral starting materials were used to obtain a racemic mixture of chiral building blocks, the spontaneous resolution of **5** may be considered as a new strategy for construction of chiral networks assisted by enantioselectively spacer-controlled self-assembly of hydrogen-bonding interactions.

In summary, we have demonstrated that both chiral and achiral three-dimensional networks with doubly interpenetrated α-polonium-related topology can be constructed from spontaneous self-assembly of chiral coordination motifs utilizing hydrogen-bonding interactions. The weak aromatic π-π interactions contribute greatly to the stabilization of this supramolecular assembly and lead to enantioselective recognition between the chiral building blocks and the spacers used. This enantioselective self-assembly process controlled by suitable spacers as presented here may

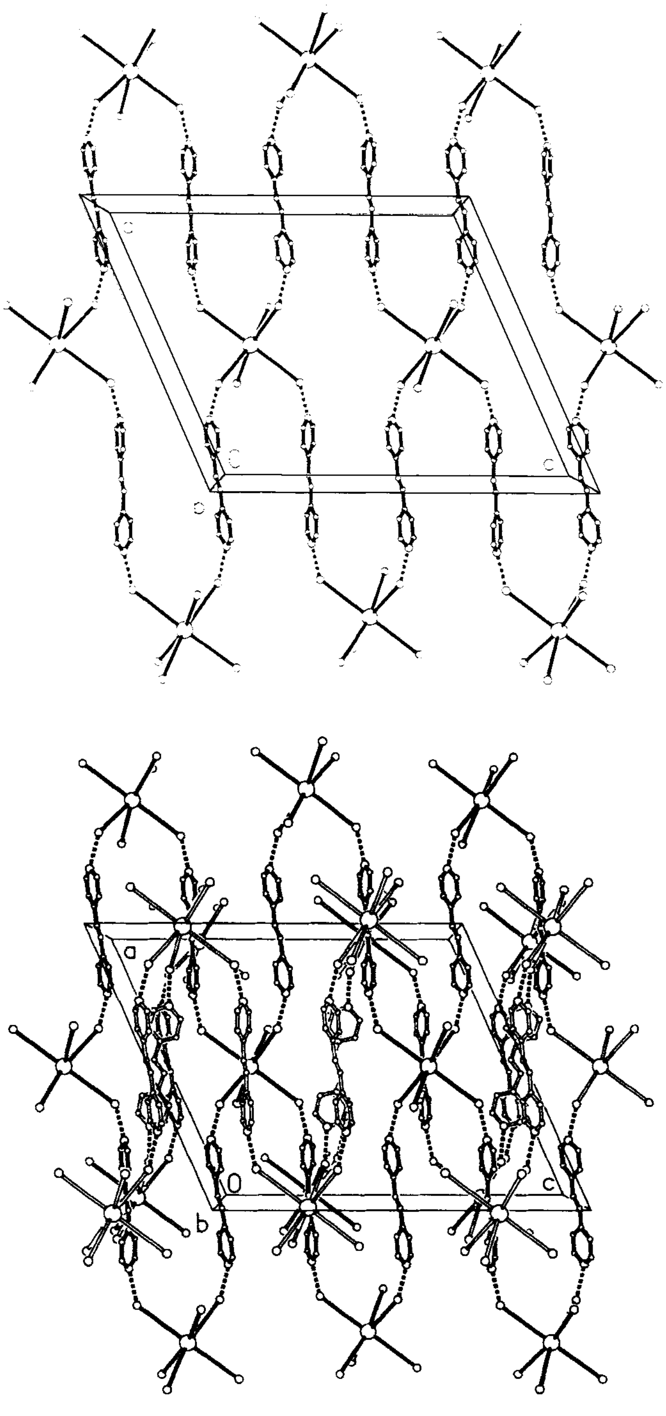


FIGURE 4 Three-dimensional frameworks in the crystal structure of **6**: (a) one independent network viewed parallel to the *b*axis; (b) doubly interlocking networks from the same perspective. For clarity, each 2-benzimidazolylmethyl arm of the ntb ligand is represented by a long rod joining each NH group to the Ln^{3+}ion. All hydrogen atoms, water molecules and perchlorate ions have been omitted. The independent interpenetrating networks are differentiated by solid and open shading

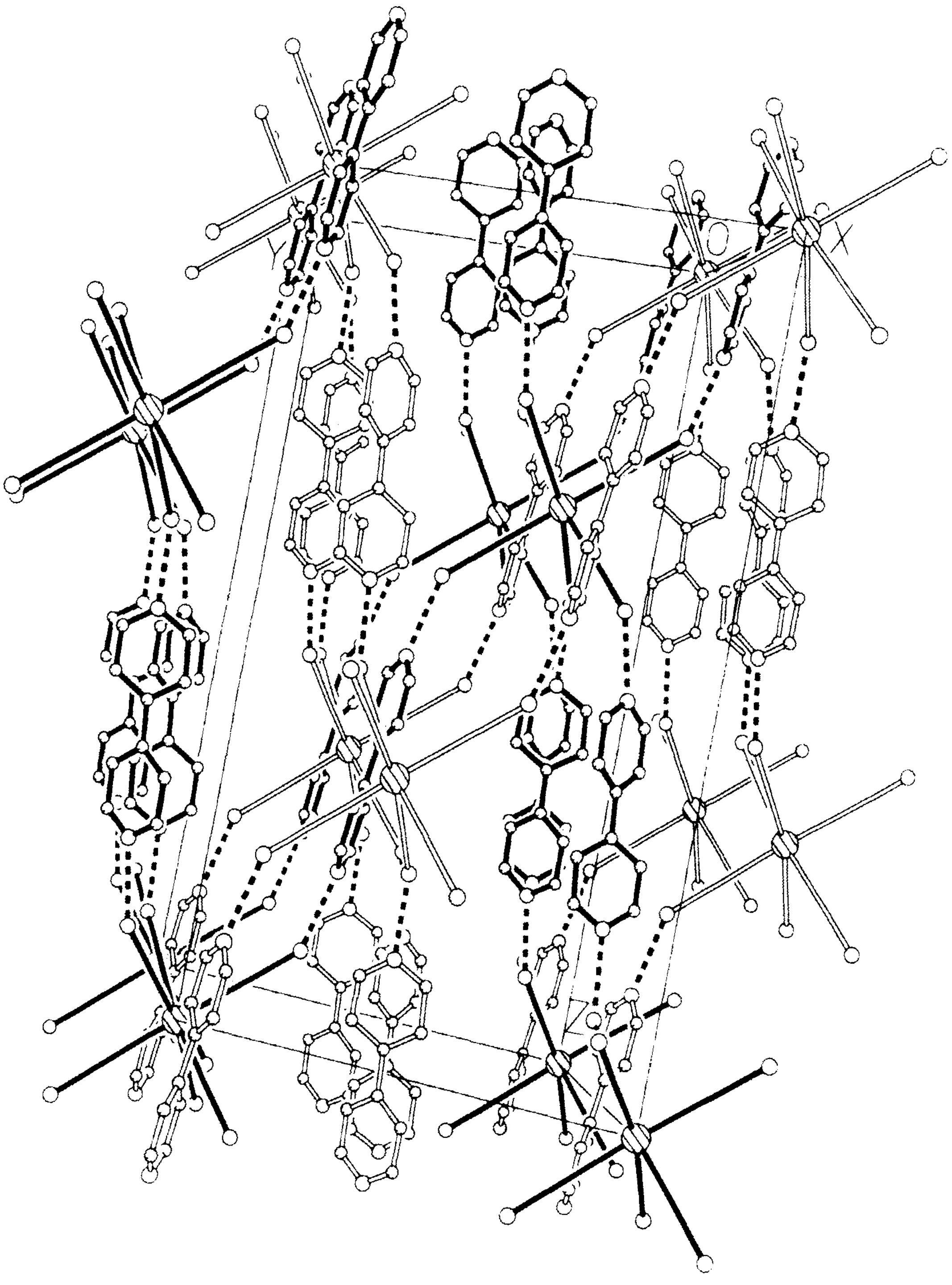


FIGURE 5 Three-dimensional doubly interlocking frameworks in the crystal structure of **5**. Representation of the supramolecular structure is simplified in the same manner as in Fig. 4

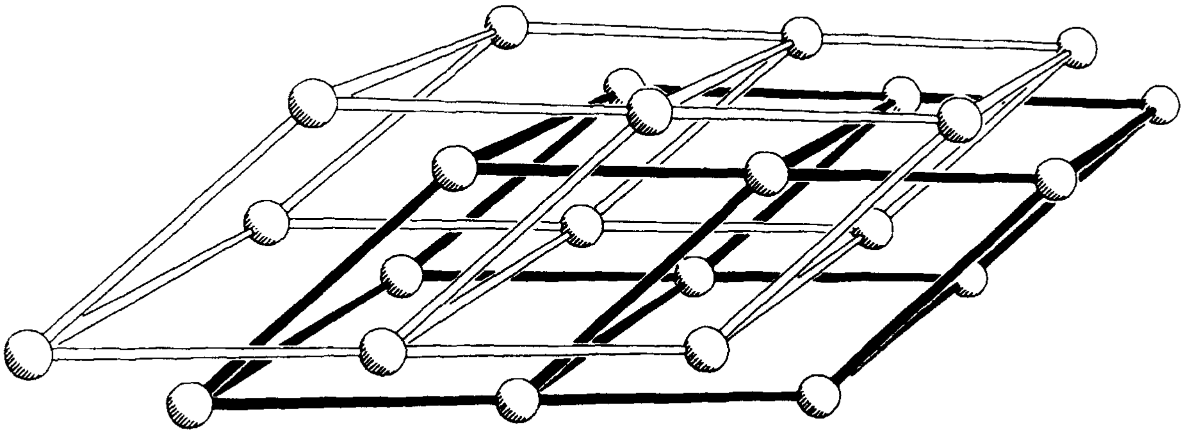


FIGURE 6 Two-fold interpenetration of α-polonium-related nets in **6**. The balls represent Nd atoms, and each rod represents a pair of 2-benzimidazolylmethyl arms and a bpen spacer that are connected by hydrogen bonds

contribute to a better understanding of enantioselective separation and the synthesis of porous chiral solids.

EXPERIMENTAL

Hydrated neodymium(III) perchlorate was prepared by dissolving the neodymium oxide (99.99%) in 30% perchloric acid. The ligand tris(2-benzimidazolylmethyl)amine (ntb) was synthesized following a slight modification of the method of Phillips by Oki *et. al.*,[19]The complexes were prepared in a similar way: hydrated neodymium(III) perchlorate was mixed with 2 equiv. of ntb in methanol, to which 3 equiv. of bipy (or bpen) dissolved in acetonitrile was added. The mixture was allowed to stand for several days to deposit a crystalline product.

Intensities were collected on a Siemens SMART CCD area detector three-circle diffractometer for **5** and a Rigaku RAXIS IIC image-plate diffractometer for **6** with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 294 K. Absorption corrections were applied using ABSCOR[20] for **6** but none for **5**. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-93 or 97 program package.[21] Information on crystal data and data collection parameters is given in Table I. In **5** the $[Nd(ntb)_2]^{3+}$ cation has exact D_3 symmetry with a C_3 axis passing through the apical nitrogen and the central Nd(III) atoms. The perchlorate anion is located on a C_2 axis and orientationally two-fold disordered. In **6** two independent bpen ligands are located at inversion centers. In the third bpen ligand that occupies a site of symmetry 2, the ethylene carbon atoms C45 and C46 exhibit disorder over two sites and were refined isotropically with half occupancy. One perchlorate anion is axially disordered about one Cl-O bond, while the other is located on an inversion center and hence orientationally two-fold disordered. The ethylene carbon atom C55 and the water oxygen atom that exhibit large thermal displacement parameters were also refined isotropically. All other non-hydrogen atoms were subjected to anisotropic refinement, while the hydrogen atoms were included in structure factor calculations with isotropic thermal parameters. The atomic parameters of **5** and **6** have been deposited with the Cambridge Crystallographic data Center as CIF files CCDC No. 129663 and 129664.

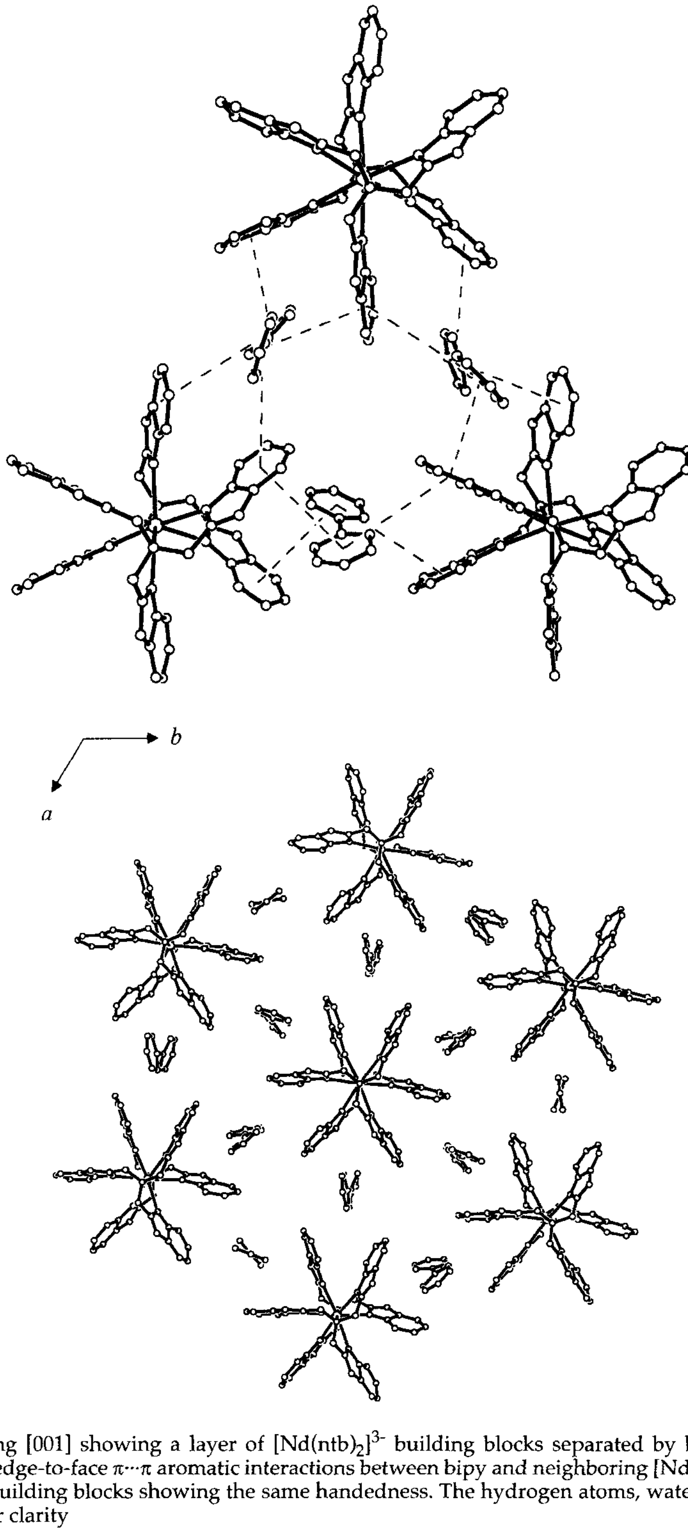


FIGURE 7 Projection along [001] showing a layer of $[Nd(ntb)_2]^{3-}$ building blocks separated by bipy spacers in complex 5: (a) weak face-to-face and edge-to-face π···π aromatic interactions between bipy and neighboring $[Nd(ntb)_2]^{3-}$ motifs; (b) hexagonal array of $[Nd(ntb)_2]^{3-}$ building blocks showing the same handedness. The hydrogen atoms, water molecule and perchlorate ions have been omitted for clarity

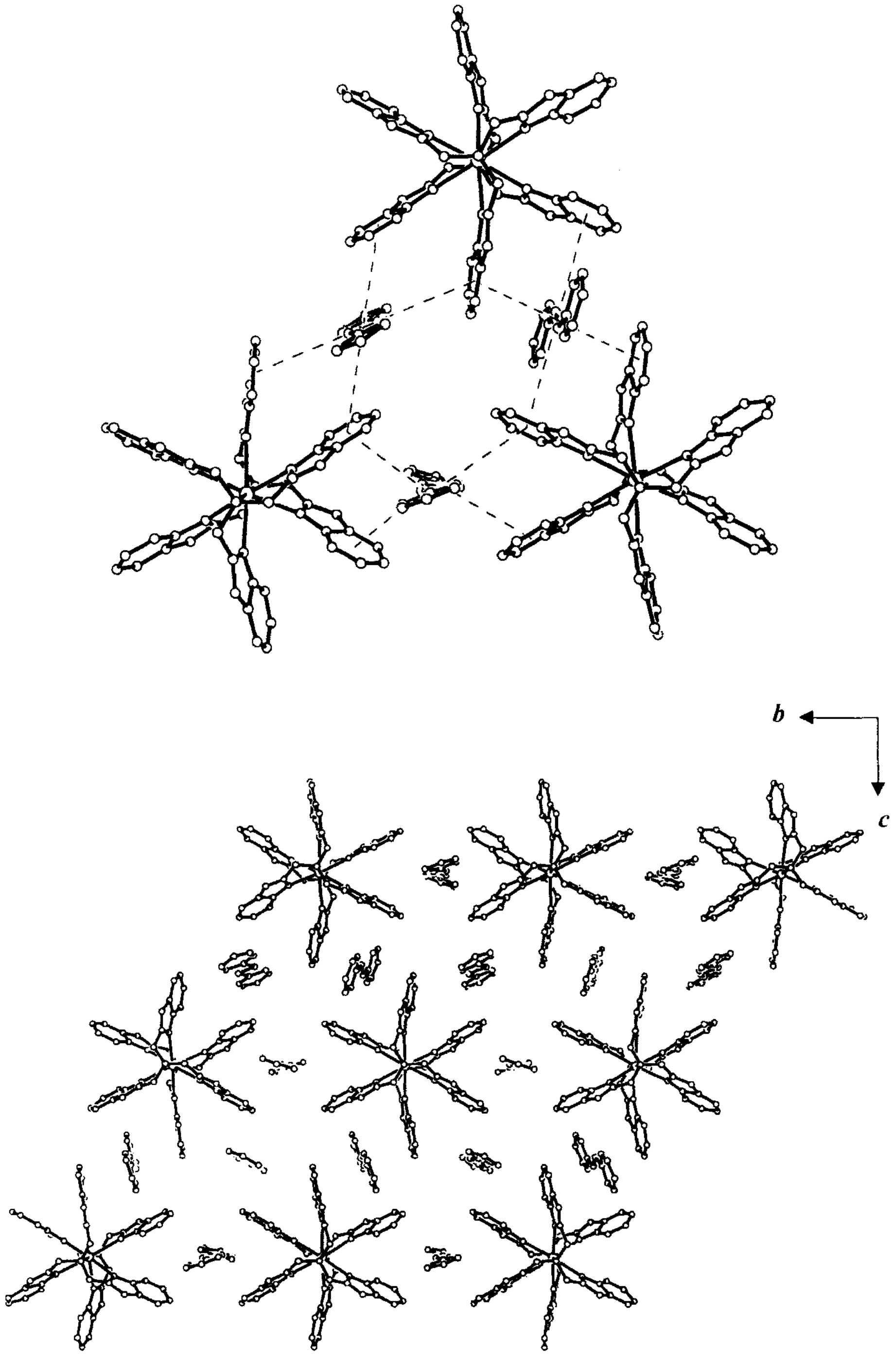


FIGURE 8 Projection along [100] showing a layer of $[Nd(ntb)_2]^{3-}$ building blocks separated by bpen spacers in complex **6**: (a) weak face-to-face and edge-to-face $\pi\cdots\pi$ aromatic interactions between the torsional and coplanar bpen spacers and neighboring $[Nd(ntb)_2]^{3-}$ motifs of the same chirality and pairs of enantiomers, respectively; (b) $[Nd(ntb)_2]^{3-}$ enantiomers arranged in alternate rows to form a racemic array. The hydrogen atoms, water molecule and perchlorate ions have been omitted for clarity

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References

1. Robson, R.; Abramhams, B. F.; Batten,S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J.; *Supramolecular Architecture*, America Chemical Society, Washington, DC, 1992; Desiraju, G. R.; *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
2. Zaworotko, M.J.; *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 1211.
3. Desiragu,G. R.; *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 2311; Melendez,R. E.; Sharma, C. V. K.; Zaworotko, M. J.; Bauer, C.; Rogers, R. D.; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2213.
4. Yaghi, O. M.; Li G.; Li, H.; *Nature*, 1995, **378**, 703; Gardner,G. B.; Venkataraman, D.; Moore, J. S.; Lee, S.; *Nature*, 1995, **374**, 792.
5. Philp, D.; Stoddart, J. F.; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1154; Stang, P. J.; *Chem. Eur. J.*; 1998, **4**, 19.
6. Olenyuk, B.; Whiteford J. A.; Stang, P. J.; *J. Am. Chem. Soc.*, 1996, **118**, 8221; Yamanari, K.; Fukuda, I.; Kawamoto, T.; Kushi, Y.; Fuyuhiro, A.; Kubota, N.; Fuhuo T.; Arakawa, R.; *Inorg. Chem.*, 1998, **37**, 5611.
7. Suárez, M.; Branda, N.; Lehn, J.-M.; De Cian, A.; Fischer, J.; *Helv. Chim. Acta*, 1998, **81**, 1.
8. Gulik-Krzywicki, T.; Fouquey, C.; Lehn, J.-M.; *Proc. Natl. Acad. Sci. U.S.A.*, 1993, **90**, 163; Bell, T. W.; Jousselin, H.; *Nature*, 1994, **367**, 441; Baum, G.; Constable, E. C.; Fenske, D.; Kulke, T.; *Chem. Commun*, 1997, 2043; Piguet, C.; Bernardinelli, G.; Hopfgartner, G.; *Chem. Rev.*, 1997, **97**, 2005, and references therein.
9. (*a*) Yaghi, O.M.; Davis, C.E.; Li, Li, G.; H.; *J. Am. Chem. Soc.*, 1997, **119**, 2861;
   (*b*) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D.; *Chem. Commun.*, 1998, 1837;
   (*c*) Kepert, C. J.; Rosseinsky, M. J.; *Chem. Commun.*, 1998, 31;
   (*d*) Abrahams,B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R.; *Chem. Commun.*, 1996, 1313;
   (*e*) Abrahams, B. F.; Coleiro, J.; Hoskins, B. F.; Robson, R.; *Chem. Commun.*, 1996, 603.
10. Stang, P. J.; *Chem. Eur. J.*, 1998, **4**, 19; Duhme, A.-K.; Davies, S. C.; Hughes, D. L.; *Inorg. Chem.*, 1998, **37**, 5380.
11. Su, C.-Y.; Kang, B.-S.; Liu, H.-Q.; Wang, Q.-G.; Mak, T. C. W.; *Chem. Commun.*, 1998, 1551.
12. Su, C.-Y.; Kang, B.-S.; Mu, X.-Q.; Sun, J.; Tong, Y.-X.; Chen, Z.-N.; *Aust. J. Chem.* 1998, **51**, 565.
13. Su, C.-Y.; Kang, B.-S.; Liu, H.-Q.; Wang, Q.-G.; Chen, Z.-N.; Lu, Z.-L.; Tong, Y.-X.; Mak, T. C. W.; *Inorg. Chem.* 1999, **38**, 1374.
14. (a) Nomenclature of Inorganic Chemistry, Recommendations 1990, Ed. by Leigh, G. J.; Blackwell, Oxford, U. K., 1990.
    (b) Knof, U.; Zelewsky, A. von; *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 302.
    (c) IUPAC Tentative Rules for the Nomenclature of Organic Chemistry, Section E, Fundamental Stereochemistry, *J. Org. Chem.*, 1970, **35**, 2849, 2857.
15. Batten, S. R.; Robson, R.; *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 1461, and references therein.
16. Hunter, C. A.; *Chem. Soc. Rev.*; 1994, 101 and references therein.
17. (a) Desiraju, G. R.; Gavezzotti, A.; *J. Chem. Soc., Chem. Commun.* 1989, 621.
    (b) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. A.; Rheingold, A. L.; Borovik, A. S.; *J. Am. Chem. Soc.*, 1996, **118**, 285.
18. Krämer, R.; Lehn, J.-M.; De Cian, A.; Fischer, J.; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 703;.
19. Oki, A. R.; Bommarreddy, P. K.; Zhang, H. M.; Hosmane, N.; *Inorg. Chim. Acta* 1995, **231**, 109.
20. Higashi, T.; ABSCOR – An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo (1995).
21. Sheldrick, G. M.; SHELX-93; SHELX-97, University of Göttingen, Germany.