A cyanide-bridged 1-D helical chain involving both four- and six-coordinate nickel(II)

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A cyanide-bridged coordination polymer, $\{[Ni(tren)][Ni(CN)_4]\}_n$ (tren = tris(2-aminoethyl)amine), has been synthesized by self-assembly of cis-$[Ni(tren)]^{2+}$ and $[Ni(CN)_4]^{2-}$ building blocks. In the molecular structure, the paramagnetic cis-$[Ni(tren)]^{2+}$ cations are bridged by diamagnetic $[Ni(CN)_4]^{2-}$ anions through two cis-cyanides to form a 1-D helical chain of $\{[Ni(tren)][Ni(CN)_4]\}_n$. The compound crystallizes with a centrosymmetrical space group, $P2_1/n$, in which the helical chains are packed in alternating right- and left-handed chiralities with a helical pitch of 10.2566(3) Å (equal to the length of the b-axis), leading to the formation of a racemic compound. The crystal packing is stabilized by moderately strong hydrogen-bonding between primary amines of tren and nitrogens of terminal cyanide.

Keywords: Synthesis; Crystal structure; Cyano-bridged nickel(II) complex; 1-D Helical chain; Thermal study

1. Introduction

Construction of helical network structures has generated a great deal of interest in coordination chemistry and crystal engineering because of their ubiquitous appearance in nature, a typical example being DNA, and for intriguing potential applications in nonlinear optical devices, enantioselective synthesis, asymmetric catalysis, and chiral magnets [1–5]. A large number of artificial helical coordination polymers, including 1-D, 2-D, and 3-D structural frameworks, have been investigated by using chiral or achiral building blocks [6–9]. The most striking feature of a helix is its chirality, however, in most cases, right-handed and left-handed helices are obtained in equal amounts as racemates when building blocks have no intrinsic chirality [10–12]. There are only a limited number of examples of spontaneous resolution in which the chiral information in enantiomeric forms of the building blocks can be transmitted into higher dimensionality to generate chiral coordination polymers [13–16].

Most supramolecular helical polymers have been constructed by the introduction of flexible organic bridging ligands which play a crucial role on the nature of the helicity [17–19]. On the other hand, helical coordination polymers involving cyanometallates

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as building units are rarely investigated, although enormous numbers of 1-D, 2-D, and 3-D polymers of such building blocks are reported [20–23]. Recently, Lu and co-workers [24, 25] investigated a few 1-D helical chains, constructed by alternate bridging of *cis*-[Ni(L)]$^{2+}$ (L = tetradentate macrocyclic ligands) with [Ni(CN)$_4$]$^{2-}$ through two *cis* cyanides, and in some cases spontaneous resolution has occurred during crystallization. It is a challenge to construct helical coordination complexes *via* combination of cyanometallates and metal cations; further research is necessary to enrich and develop this field.

I focus my attention on obtaining new helical coordination polymers *via* linking transition metal cations with [Ni(CN)$_4$]$^{2-}$. Helical chain structures can conveniently be achieved when two *cis* coordination positions of metal cations are available for further coordination. Treatment of tetradentate tripodal ligands with nickel(II) produce *cis*-octahedral configuration making them promising building blocks for the synthesis of helical coordination polymers. In this work, I selected tris(2-aminoethyl)amine (tren) as an ancillary ligand, and self-assembly of *cis*-[Ni(tren)]$^{2+}$ and [Ni(CN)$_4$]$^{2-}$ units, leading to the construction of a 1-D helical chain of {[Ni(tren)][Ni(CN)$_4$]}$_n$.

2. Experimental

2.1. *Materials and methods*

All chemicals and solvents were of reagent grade and used as received. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. FTIR spectra were recorded from 400 to 4000 cm^{-1} on a Nicolet 750 Magna-IR spectrometer using KBr pellets. Magnetic susceptibility was measured at 27°C using an EG and G PAR-155 vibrating sample magnetometer with Hg[Co(SCN)$_4$] as reference; diamagnetic corrections were made by Pascal's constants for all the constituent atoms. Thermal analyses were carried out on a Perkin-Elmer Pyris Diamond system.

2.2. *Synthesis of the complex {[Ni(tren)][Ni(CN)$_4$]}$_n$*

A mixture of Ni(NO$_3$)$_2$ · 6H$_2$O (58.16 mg, 0.2 mmol) and tren (29.25 mg, 0.2 mmol) in 5 mL of CH$_3$OH was stirred for 20 min. The resulting solution was placed in one arm of an H-shaped tube. A solution of K$_2$Ni(CN)$_4$ (48.2 mg, 0.2 mmol) in 5 mL of water was added in other arm and the rest of the tube was carefully filled with methanol–water solution. Slow diffusion over a period of about 3 weeks produced block-shaped purple crystals of the complex suitable for X-ray diffraction. Yield: 38.2 mg, 52%. Anal. Calcd for C$_{10}$H$_{18}$N$_8$Ni$_2$: C, 32.63; H, 4.89; N, 30.45. Found (%): C, 32.78; H, 4.82; N, 30.19. IR (KBr, cm^{-1}): 3150s (ν_{NH}); 2865w (ν_{CH}); 2120s and 2154s (ν_{CN}).

2.3. *X-ray crystallography*

X-ray diffraction data for the complex were collected on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A crystal of approximate dimensions 0.30 × 0.25 × 0.15 mm^3 was

Table 1. Crystal data and structure refinement of the complex.

Empirical formula	$C_{10}H_{18}N_8Ni_2$
Formula weight	367.74
Temperature (K)	145(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	12.0556(3)
b	10.2566(3)
c	13.6558(4)
β	113.972(10)
Volume (Å^3), Z	1542.89(7), 4
Calculated density (g cm^{-3})	1.583
Absorption coefficient (mm^{-1})	2.443
$F(000)$	760
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.15$
θ range for data collection (°)	3.53–27.50
Limiting indices	$-15 \le h \le 15$; $-11 \le k \le 13$; $-17 \le l \le 17$
Reflections collected/unique	6083/3027 [R(int) = 0.0292]
Completeness to 2θ (%)	99.5
Data/restraints/parameters	3520/0/235
Max. and min. transmission	0.8285 and 0.5692
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0256$, $wR_2 = 0.0585$
R indices (all data)	$R_1 = 0.0326$, $wR_2 = 0.0612$
Largest difference peak/hole (e Å^{-3})	0.351 and -0.459

mounted on a glass fiber using N-Paratone oil and cooled *in situ* using an Oxford Cryostream 600 Series to 145 K for data collection. Intensities were integrated by using DENZO-SMN and scaled with SCALEPACK [26]. Several scans in φ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares based on F^2 using the SHELXL-97 [27] program within the WINGX package [28]. Hydrogens were located in a difference Fourier map and their isotropic thermal parameters were tied with their respective parent atoms [$U(H) = 1.5U(N)$ or $1.5U(C)$]. Hydrogens were refined isotropically. Further details of the structural analysis are given in table 1.

3. Results and discussion

3.1. *Synthesis and general characterization*

Single crystals were grown in a water–methanol solution by slow diffusion using an H-shaped tube. Self-assembly of *cis*-[Ni(tren)]$^{2+}$ and [Ni(CN)$_4$]$^{2-}$ afforded block-shaped purple crystals of [Ni(tren)][Ni(CN)$_4$] in good yield. This compound is very stable in air and is almost insoluble in common solvents, such as water, alcohol, acetonitrile, chloroform, and acetone. The composition of the complex is confirmed by elemental analysis. To study the stability of the polymer, thermogravimetric analysis

(TGA) was performed revealing that the complex is stable to 280°C and then decomposes rapidly. Further details of TGA have been described in a following section.

3.2. *Description of the crystal structure*

The structure of the complex has been determined by single-crystal X-ray diffraction. Crystallographic data and details of the data collection for the complex are listed in table 1, and selected bond lengths and angles are summarized in table 2. The complex crystallizes in the monoclinic $P2_1/n$ space group without the presence of solvent. The molecular structure of the complex is depicted in figure 1 with the atom labeling schemes. The asymmetric unit consists of one *cis*-[Ni(tren)]$^{2+}$ and one [Ni(CN)$_4$]$^{2-}$ interlinked by bridging cyanide. The coordination geometry of Ni(II) in *cis*-[Ni(tren)]$^{2+}$ is slightly distorted octahedral, from four nitrogens of the tripodal tren and two

Table 2.   Selected bond lengths (Å) and angles (°) for the complex.

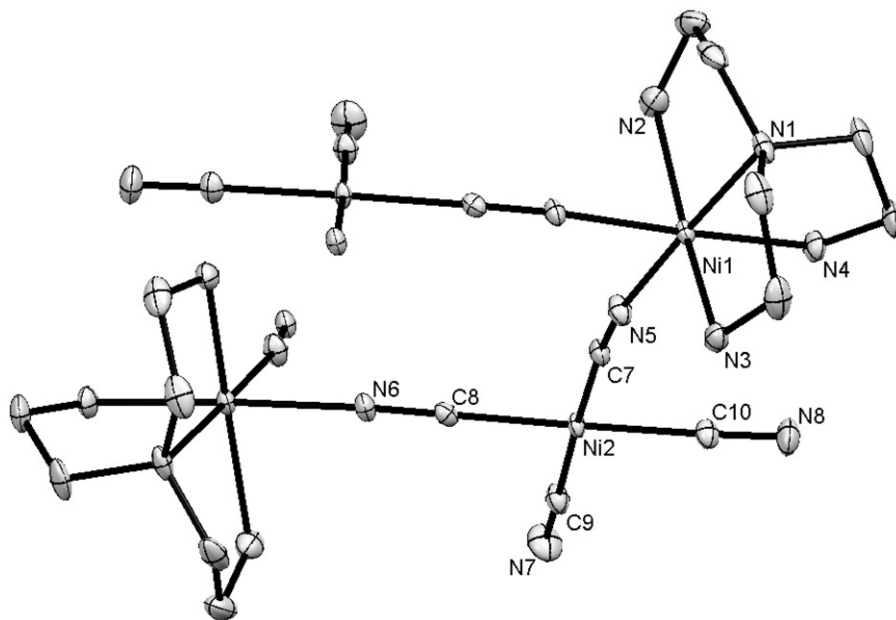| Ni1–N1	2.086(2)	Ni1–N2	2.125(2)
Ni1–N3	2.112(2)	Ni1–N4	2.102(2)
Ni1–N5	2.040(2)	Ni1–N6	2.114(2)
Ni2–C7	1.860(2)	Ni2–C8	1.865(2)
Ni2–C9	1.871(2)	Ni2–C10	1.864(2)
C7–N5–Ni1	166.6(2)	C8–N6–Ni1	157.0(2)
N5–C7–Ni2	175.4(2)	N6–C8–Ni2	176.5(2)
N7–C9–Ni2	179.0(2)	N8–C10–Ni2	177.8(2)

Figure 1.   Molecular structure of the complex. Thermal ellipsoids are drawn in 30% probability and hydrogens have been omitted for clarity.

nitrogens of bridging cyanides in a *cis* configuration. The Ni–N bond distances for tren vary from 2.086(2) Å (Ni1–N1) to 2.125(2) Å (Ni1–N2), while Ni–N(cyanide) are 2.040(2) and 2.114(2) Å. The Ni(II) in $[Ni(CN)_4]^{2-}$ displays square planar geometry from four cyanides with Ni–C bond distances ranging from 1.860(2) Å (Ni2–C7) to 1.871(2) Å (Ni2–C9); all bond lengths are in normal range and are comparable to literature reported values of similar complexes [29–34]. Deviation of Ni2 from the mean square plane, defined by Ni2, C7, C8, C9, and C10, is 0.009 Å, whereas maximum deviations observed for C8 and N6 are 0.008 and 0.053 Å, respectively. The bridging mode of Ni1–C≡N–Ni2 is nonlinear. The Ni1–C≡N bond angles for bridging cyanides, 175.4(2)° and 176.5(2)°, deviate slightly from linearity, while Ni–N≡C angles are 166.6(2)° and 157.0(2)°, showing significant deviation from the ideal geometry, which might be due to steric interactions between terminal cyanides and tripodal tren. The metal···metal separations across the bridging cyanides are 4.997(4)° and 5.011(4)°, consistent with literature reported values of $[Ni(CN)_4]^{2-}$-bridged nickel(II) complexes [35–42].

In the extended structure, the $[Ni(CN)_4]^{2-}$ alternatively bridge *cis*-$[Ni(tren)]^{2+}$ through their two *cis* cyanides to construct a 1-D chain structure along the *b*-axis. Two adjacent $[Ni(CN)_4]^{2-}$ planes are non-planar, twisted to avoid the repulsive interactions among the uncoordinated cyanide groups with a dihedral angle of 55.2°. The twisted arrangements generate a 1-D chiral helical chain along the crystallographic 2_1 screw axis, running parallel to the *b*-axis. The pitch of the helical chain is just one unit cell length along the *b*-axis, 10.2566(3) Å. However, two adjacent helices with alternating right- and left-handed chiralities, which are centro-symmetrically related to each other, are packed together along the *b*-axis leading to racemic helical polymers (figure 2).
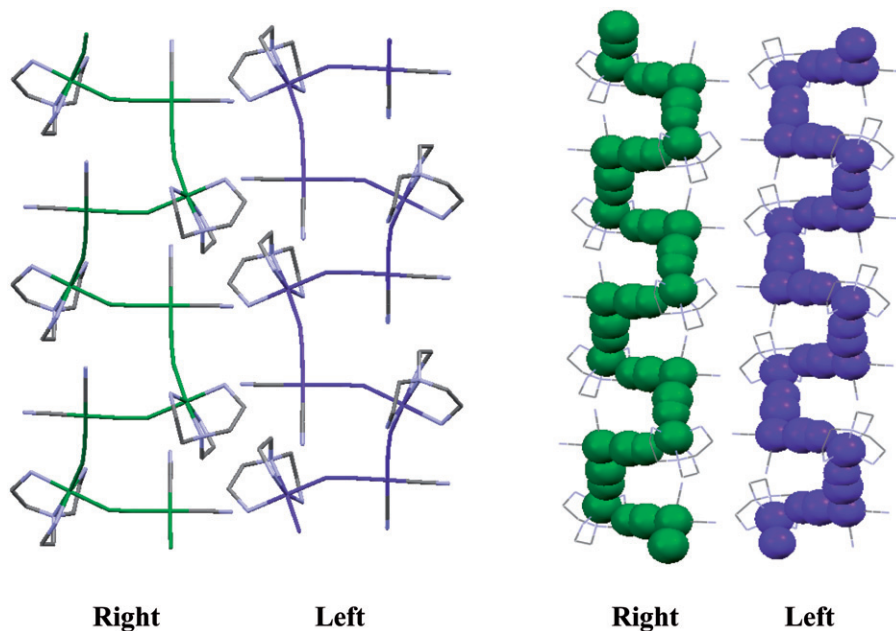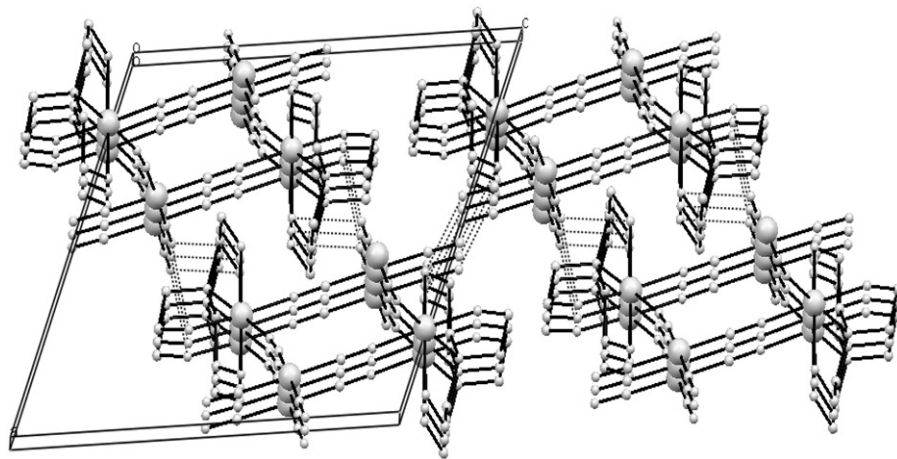

Right   **Left**   **Right**   **Left**

Figure 2.   Perspective view of the 1-D helical chains of right- and left-handed chiralities.

Table 3. Important hydrogen bonds (Å and °) for the complex.

D–H···A	d(D–H)	d(H···A)	d(D···A)	$\angle$(DHA)
N2–H2D···N7	0.89	2.44	3.171(3)	147
N3–H3C···N8	0.89	2.10	2.970(3)	167
N4–H4D···N7	0.85	2.36	3.182(3)	165

Figure 3. Molecular packing of the complex, viewed along the *b*-axis, showing the intermolecular hydrogen-bonding interactions.

The left- and right-handed helices have strong hydrogen-bonding involving primary amines of tren and nitrogens of $[Ni(CN)_4]^{2-}$ from adjacent chains (table 3 and figure 3). The shortest interchain Ni···Ni distances of 6.234(4) and 6.538(4) Å are longer than their intrachain separations (see above). Another interesting aspect of the present compound is that similar homochiral chains are stacked along the *c*-axis (figure 4) with the helix-to-helix separation of 13.6558(4) Å, which is equal to the length of the *c*-axis. The structural feature of this compound can be compared with the reported structures of Lu and co-workers [24, 25], but the key difference is that instead of a macrocyclic ligand a simple tetradentate tripodal ligand has been introduced in the present work. The easiest way to construct 1-D helical polymer is to assemble $[Ni(CN)_4]^{2-}$ with coordinated metal cations having two *cis* positions available for two bridging cyanides. Therefore, a tetradentate tripodal ligand could be the most fascinating choice in this regard as it produces an octahedral nickel(II) in which two *cis* positions are available for further coordination. Although there are several reports on $[Ni(CN)_4]^{2-}$-bridged homobimetallic polymeric chains in the literature, to the best of my knowledge tetradentate tripodal ligands have never been employed for such syntheses.

3.3. *IR spectroscopy and magnetic properties*

The most important features of the IR spectrum involve characteristic CN stretching frequencies. Formation of cyanide bridges in the polynuclear complexes was shown by
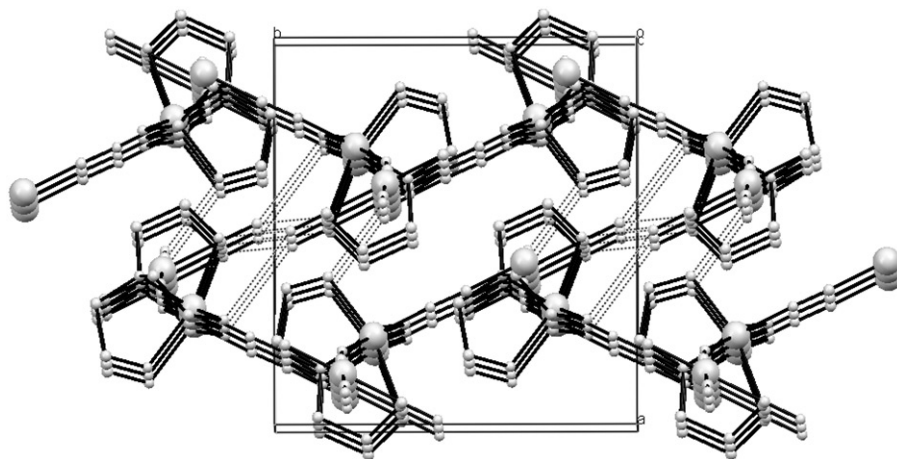
Figure 4.   Molecular packing of the complex, viewed along the *c*-axis, showing the alternating stack of left-and right-handed helices.

the stretching vibration of cyanides. The complex exhibits two strong bands at 2154 and 2120 cm^{-1}, attributable to C≡N stretching vibrations. The splitting of the C≡N stretching band compared to K$_2$[Ni(CN)$_4$] (2127 cm^{-1}) indicates the presence of terminal and bridging cyanides. Formation of a cyanide bridge shifts $\nu_{C≡N}$ to higher frequencies. The strong band at 2154 cm^{-1} may, therefore, be attributed to $\nu_{C≡N}$ of bridging cyanides and that at 2120 cm^{-1} to terminal ones. In addition to the cyanide stretch the spectrum shows a broad band at 3150s cm^{-1}, which may be assigned to $\nu_{N–H}$ of tren. The broadening is due to the involvement of primary amines of tren in strong hydrogen-bonding, stabilizing the crystal packing. A relatively weak band at 2865 w cm^{-1} due to $\nu_{C–H}$ has also been observed. There is no band at 1384 cm^{-1} for symmetric stretching of NO$_3^-$, indicating the neutral nature of the helical chain, consistent with the crystal structure of the complex.

The room temperature magnetic susceptibility measurement was carried out on a PAR 155 vibrating sample magnetometer with a field of 5000 G. The effective magnetic moment (μ_{eff}) per Ni(II) dimer is 2.78 BM, indicating octahedrally coordinated para-magnetic Ni(II) ions (S = 2) are well-isolated by diamagnetic square planar Ni(II) (S = 0).

3.4. *Thermogravimetric analysis*

To examine the thermal stability of the complex, TG-DTA analyses have been performed under dynamic air at a heating rate of 10 min^{-1} between 25°C and 700°C. The TG curve (figure 5) clearly indicates that the compound is stable to 280°C and then decomposes rapidly. The decomposition has been observed in two consecutive steps. The first is accompanied with an endothermic peak at 308°C and a total mass loss of 39.05% from 280°C to 352°C, ascribed to elimination of coordinated tren from nickel(II) (Calcd 39.76%). The second decomposition step starts with a broad exothermic effect at 437°C, assigned to degradation of cyanide. At about 620°C, it decomposed completely and the remaining residue is presumed to be NiO (Calcd 40.62%; Found: 40.91%).
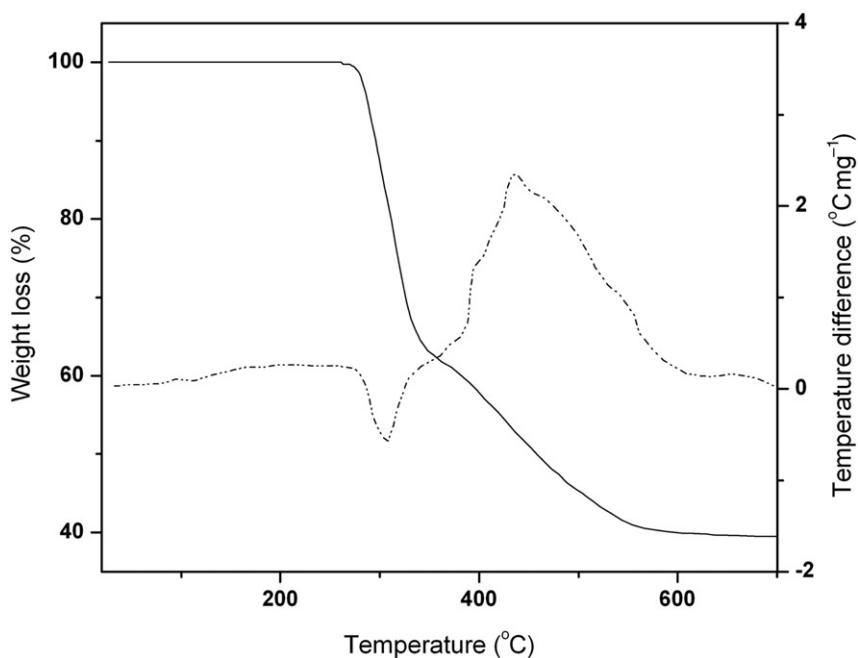
Figure 5.   TGA (–) and DTA(···) curves of the complex at a heating rate of $10°C$ min^{-1}.

4. Concluding remarks

A cyanide-bridged 1-D helical coordination polymer of nickel(II) has been synthesized and structurally characterized. The twisted arrangements of adjacent $[Ni(CN)_4]^{2-}$ lead to the formation of a 1-D helical chain with left- and right-handed helices present in equal numbers and, therefore, giving rise to an overall racemic compound. Further research involving spontaneous chiral resolution upon crystallization of similar complexes with other tripodal ligands is in progress.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 796672). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336033; E-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

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