

catena-Poly[[bis(hexafluoroacetylacetonato- κ^2O,O')zinc(II)]- μ -4,4'-bipyridine- $\kappa^2N:N'$]

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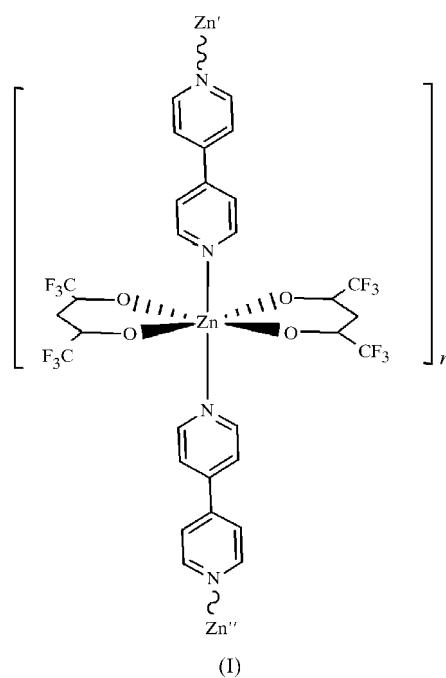
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The structure of the title compound, *catena*-poly[[bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato- κ^2O,O')zinc(III)]- μ -4,4'-bipyridine- $\kappa^2N:N'$], $[Zn(C_5HF_6O_2)_2(C_{10}H_8N_2)]_n$, consists of polymeric chains, running in two perpendicular directions, organized as planes normal to the tetragonal axis. The elemental unit of the chains is the zinc(II) coordination polyhedron bisected by a twofold symmetry axis, and thus only half of the unit is independent. The octahedral coordination geometry of the metal centre is composed of two oxygen-chelating (symmetry-related) hexafluoroacetylacetone groups and two translationally related 4,4'-bipyridine groups, which act as connecting agents in the polymer structure. The stabilization of this architecture of chains and planes is associated with a number of weak C—H···O and C—H···F hydrogen bonds.

Comment

Coordination polymers with exo-bidentate (divergent) bridging ligands, such as 4,4'-bipyridine, have been prepared *via* self-assembly reactions, and when the ligand-to-metal ratio is 1:1, one-dimensional polymers are produced (Roesky & Andruh, 2003). The zinc(II) species $Zn(hfac)_2 \cdot 2H_2O$ (hfac is the hexafluoroacetylacetone anion) exhibits a high affinity towards divergent bis(4-pyridyl)-based ligands (*L*), giving crystalline polymeric compounds of formula $[Zn(hfac)_2(L)]$ (Ellis *et al.*, 2000; Matsuda *et al.*, 2001; Horikoshi *et al.*, 2002). The coordination environment around the metal centres is [4+2]-octahedral, with either *cis* (Ellis *et al.*, 2000) or *trans* (Matsuda *et al.*, 2001; Horikoshi *et al.*, 2002) configurations of the coordinated 4-pyridyl rings, forming helical and linear infinite chains, respectively. To our knowledge, the only known

crystal structure of a one-dimensional polymer containing the bridging ligand 4,4'-bipyridine and the hfac anion is that of the manganese(II) complex *cis*- $[Mn(hfac)_2(4,4'-bipyridine)]$. In this compound, the structure consists of zigzag chains in which the metal centre is bridged by the 4,4'-pyridine ligand (Shen *et al.*, 1998; Plater *et al.*, 2000). We report here the structural behaviour of the new 4,4'-bipyridine-based coordination polymer *trans*- $[Zn(hfac)_2(4,4'-bipyridine)]_n$, (I). This polymer contains linear chains, ordered in a parallel fashion to produce stacking layers at 90° to one another. A plausible explanation of this somewhat unusual design is given by considering the enhanced acidity of all types of CH moieties; this enhancement is due to the presence of N and F atoms in the ligands (Thalladi *et al.*, 1998), which produce a combination of intra-polymeric (Baird *et al.*, 1999) and interpolymeric (Desiraju, 1996; Thalladi *et al.*, 1998; Dong *et al.*, 1999; Dautel & Fourmigue, 2000) C—H···O and C—H···F hydrogen bonds.



The complex crystallizes in the tetragonal space group $P4_32_12$. The structure consists of polymeric chains running in two perpendicular directions, *viz.* along [110] (at $z = 0$ and $\frac{1}{2}$) and along $[\bar{1}\bar{1}0]$ (at $z = \frac{1}{4}$ and $\frac{3}{4}$) (Fig. 1). These chains are built up around a family of twofold axes that bisect the elemental Zn octahedra, thus rendering only half of the units independent. The basal coordination plane of this octahedron is formed by two symmetry-related hexafluoroacetylacetone groups that bind the cation *via* both O atoms in a chelating mode (Fig. 2). The apical sites are, in turn, occupied by terminal N atoms from two translationally related 4,4'-bipyridine moieties, which act as connecting links that give rise to the polymeric chains.

The resulting polyhedra are quite regular; the four equatorial O atoms deviate from planarity by less than 0.04 Å, leaving the cation 0.067 Å away along the twofold axis perpendicular to the plane. The basal bonds span the tight

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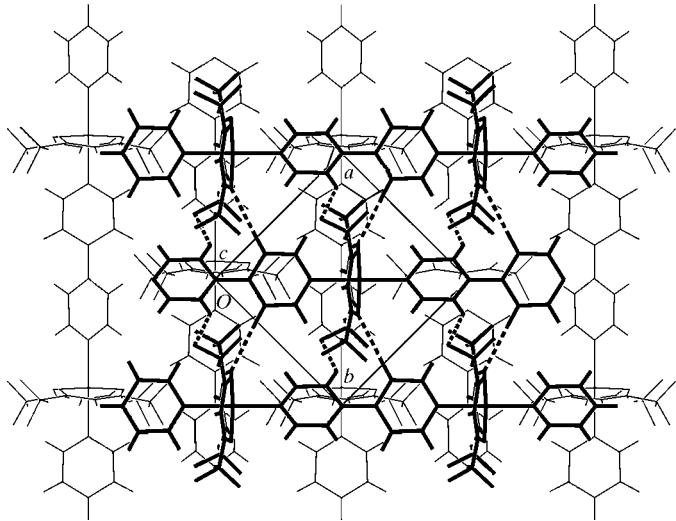


Figure 1

A packing view of (I) along the c axis, showing the organization of chains into planes parallel to (001). The plane at $z \approx \frac{1}{4}$ (top) is drawn using heavy lines, while the plane at $z \approx \frac{1}{2}$ (below) is represented by lighter lines. Note that chains in one plane are perpendicular to those in the neighbouring plane. Class B hydrogen bonds, linking chains into planes, are represented by broken lines; these are only shown in the top plane for clarity. For symmetry codes, refer to Table 2.

range 2.079 (3)–2.092 (3) Å, while the apical bonds are longer and differ slightly more [2.142 (4) and 2.191 (4) Å]. The basal angles, in turn, deviate from ideal values by less than 2% (Table 1). In spite of the internal regularity of the innermost coordination shell, the hexafluoroacetylacetone groups (the non-fluorine core is planar within 0.015 Å) bind in a slightly slanted way, subtending an angle of 14.5° to the basal plane and thus giving the Zn environment a concave shape. The two planar groups of the 4,4'-bipyridyl ligand are rotated with respect to one another by 35.5°, the ligand binding *via* atom N1B being almost exactly parallel to one of the ‘vertical’ coordination planes.

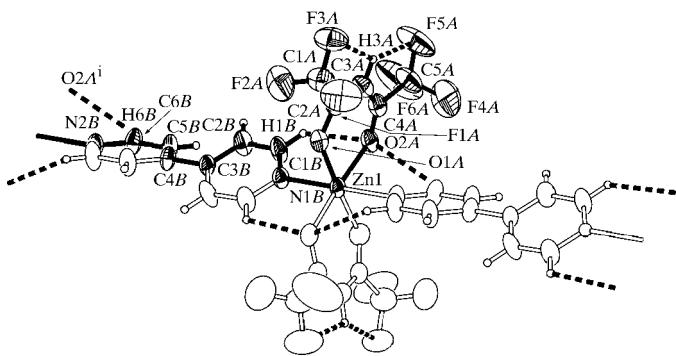


Figure 2

A molecular diagram of (I), showing how the chains are formed. The atomic numbering scheme is shown only in the independent part of the coordination polyhedron, which is drawn with displacement ellipsoids at the 40% probability level. Hydrogen-bonding interactions within the chain (class A) are shown as broken lines. For symmetry codes, refer to Table 2.

As expected from the lack of efficient H-atom donors of the OH or NH type, there are no strong hydrogen-bonding interactions in the structure. However, as mentioned above, the presence of N- and F-containing ligands tends to enhance the acidity of the CH moieties, favouring the formation of a number of C—H \cdots X ($X = O$ and F) contacts, which are largely responsible for packing stabilization. For clarity in the following discussion, we define three different ‘classes’ of bonds, grouped according to their role in the three-dimensional connectivity and with no further signification regarding type or quality (see Table 2). The first four (class A contacts; Fig. 2) are intrachain interactions, which serve to inhibit the otherwise free rotation of the CF₃ groups (*via* two C—H \cdots F bonds involving the hfac methyne H atom and two F atoms from two adjacent electron-withdrawing CF₃ groups) and the 4,4'-bipyridine bases (*via* two C—H \cdots O contacts involving aromatic CH groups and hfac O atoms). In this group of weak hydrogen bonds, all D—H \cdots A angles are small because of the restraints imposed by the intramolecular geometry. Similar values, however, have been reported (Baird *et al.*, 1999) for comparable interactions.

The second group (class *B*; Fig. 1) involves one C—H···F and one C—H···O interaction, which link the chains to one another [a similar case was reported by Dong *et al.* (1999)], thus forming two-dimensional arrays parallel to (001) (see discussion below). The third group (class *C*; in fact, only one C—H···F interaction; Fig. 3) contributes to the interplanar stability.

The relative importance of the ‘in-plane’ [parallel to (001)] and ‘out-of-plane’ [normal to (001)] interactions is clearly reflected in the different interchain spacings resulting from the action of these interactions; when traversing the structure along a base diagonal ([110] or $\bar{[1}10]$ directions), the mean chain separation is $a/1.4142$ or $\sim 5.7 \text{ \AA}$. This value is much

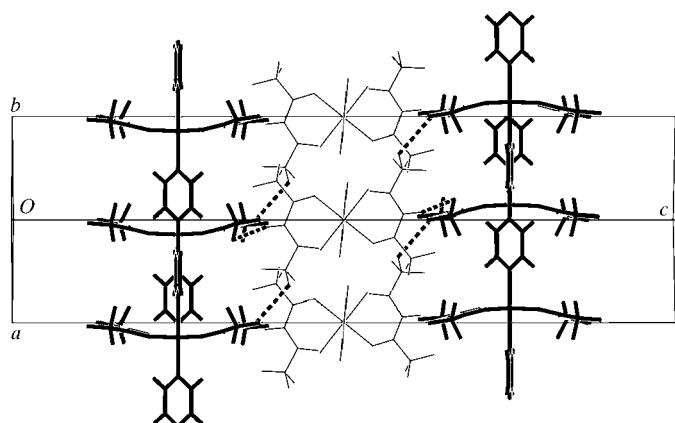


Figure 3

A packing view of (I) along a base diagonal, at a right angle to the direction used in Fig. 1, showing in projection the two-dimensional structures parallel to (001). The planes at $z \approx \frac{1}{4}$ and $\frac{3}{4}$ are shown using heavy lines (chains running vertically in the plane of the figure); lighter lines represent the plane at $z \approx \frac{1}{2}$ (chains coming out of the plane of the figure). Class C C—H \cdots F contacts, linking planes, are shown as broken lines. For symmetry codes, refer to Table 2.

smaller than that found when traversing the structure along the *c* axis (mean separation = *c*/4 or ~ 9.1 Å). This fact justifies the description of the packing scheme as being formed by alternate planes parallel to (001), those at *z* = 0 and $\frac{1}{2}$ having their ‘weave’ running along [110], and those at *z* = $\frac{1}{4}$ or $\frac{3}{4}$ running in the orthogonal [−110] direction.

It appears that the peculiar stacking of the two-dimensional structures enables a closer approach of planes, allowing some extremely weak, but nonetheless stabilizing, C—H···F contacts (class *C* in our terminology) to form. This argument receives further support when the above structure is compared with those of the related acetylacetone (acac) complexes [*M*(4,4'-bipyridine)(acac)₂]_{*n*} (*M* = Co^{II} and Cu^{II}; Ma *et al.*, 2001; Shi & Xu, 1985), where the replacement of −CF₃ groups by −CH₃ moieties produces polymeric chains running only in one direction. Thus, it seems that in the hexafluoroacetyl-acetonate complex [Zn(hfac)₂(4,4'-bipyridine)]_{*n*}, the chains try to accumulate in such a way as to optimize the viability of C—H···F interactions.

Experimental

For the synthesis of *trans*-[Zn(hfac)₂(4,4'-bipyridine)], a methanol solution (15 ml) of Zn(hfac)₂·2H₂O (0.052 g, 0.10 mmol, Aldrich) was added into a solution of 4,4'-bipyridine (0.016 g, 0.10 mmol, Merck) in methanol (3 ml). The resulting solution was stirred for 0.5 h, and the white crystalline precipitate was washed with methanol (3 × 2.5 ml) and dried *in vacuo*. Single crystals suitable for X-ray diffraction were obtained by recrystallization from methanol. Analysis calculated for C₂₀H₁₀F₁₂N₂O₄Zn: C 37.79, H 1.59, N 4.41%; found: C 37.75, H 1.68, N 4.63%.

Crystal data

[Zn(C₅HF₆O₂)₂(C₁₀H₈N₂)]
*M*_r = 635.67
 Tetragonal, *P*4₃2₁2
a = 8.0612 (4) Å
c = 36.648 (3) Å
V = 2381.5 (3) Å³
Z = 4
*D*_x = 1.773 Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 234 reflections
 θ = 3.1–22.3°
 μ = 1.16 mm⁻¹
T = 297 (2) K
 Plate, colourless
 0.30 × 0.28 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2000)
 T_{\min} = 0.71, T_{\max} = 0.87
 20 037 measured reflections

2791 independent reflections
 2134 reflections with $I > 2\sigma(I)$
 R_{int} = 0.070
 θ_{\max} = 28.2°
 h = −10 → 10
 k = −10 → 10
 l = −46 → 46

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.048
 $wR(F^2)$ = 0.132
 S = 0.94
 2791 reflections
 180 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.089P)^2 + 0.1176P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002
 $\Delta\rho_{\max}$ = 0.37 e Å⁻³
 $\Delta\rho_{\min}$ = −0.23 e Å⁻³
 Absolute structure: Flack (1983),
 982 Friedel pairs
 Flack parameter = 0.30 (3)

Table 1
 Selected geometric parameters (Å, °).

Zn1—O2A	2.079 (3)	Zn1—N1B	2.142 (4)
Zn1—O1A	2.092 (3)		
O2A—Zn1—O2A ^v	176.08 (15)	O1A—Zn1—N1B	91.73 (8)
O2A—Zn1—O1A	88.36 (11)	O2A—Zn1—N2B ^{vi}	88.04 (8)
O2A ^v —Zn1—O1A	91.52 (11)	O1A—Zn1—N2B ^{vi}	88.27 (8)
O1A—Zn1—O1A ^v	176.55 (16)	N1B—Zn1—N2B ^{vi}	180.0
O2A—Zn1—N1B	91.96 (8)		

Symmetry codes: (v) 1 − *y*, 1 − *x*, $\frac{3}{2} - z$; (vi) 1 + *x*, *y* − 1, *z*.

Table 2
 Short-contact and hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
Intrachain data (A)				
C3A—H3A···F3A	0.96	2.36	2.730 (6)	102
C3A—H3A···F5A	0.96	2.36	2.739 (6)	103
C1B—H1B···O2A	0.96	2.44	3.064 (5)	123
C6B—H6B···O2A ⁱ	0.96	2.64	3.115 (5)	111
Intraplane data (B)				
C2B—H2B···F1A ⁱⁱ	0.96	2.71	3.430 (6)	132
C5B—H5B···O2A ⁱⁱⁱ	0.96	2.81	3.620 (5)	143
Interplane data (C)				
C3A—H3A···F6A ^{iv}	0.96	2.92	3.771 (6)	148

Symmetry codes: (i) *x* − 1, 1 + *y*, *z*; (ii) *x* − 1, *y*, *z*; (iii) −*y*, 1 − *x*, $\frac{3}{2} - z$; (iv) $\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{5}{4} - z$.

H atoms attached to C atoms were placed at calculated positions and allowed to ride on their parent atoms. The C—H distance used for the refinement was 0.96 Å, *viz.* the *SHELXL*97 (Sheldrick, 1997) default distance. In all cases, *U*_{iso}(H) values were taken to be 1.2*U*_{eq} of the attached C atom. The structure was refined as a racemic twin with a ratio of 0.70 (3):0.30 (3).

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1228). Services for accessing these data are described at the back of the journal.

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