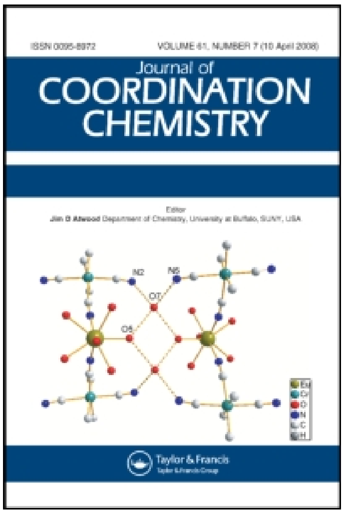

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Rheological phase synthesis, characterization and magnetic property of a cobalt(II)diphosphonate

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Rheological phase synthesis, characterization and magnetic property of a cobalt(II)diphosphonate

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A new Co(II) diphosphonate compound, $[Co(HEDPH_2)_2]$ $(4,4'\text{-bipyH}_2)\cdot H_2O$ (**1**) has been successfully obtained by a rheological phase reaction at 80°C. Single-crystal diffraction analysis shows a 1-D chain structure and the 1-D chains are assembled via hydrogen bonds into a 3-D supramolecular structure with channels. The protonated 4,4′-bipy molecules are encapsulated in the channels. Magnetic study shows **1** to exhibit antiferromagnetic interaction in the 1D Co–O–P–O–Co chain. Crystal data for **1**: monoclinic, space group *Cc*, $a = 15.754(6)$ Å, $b = 14.457(5)$ Å, $c = 10.020(4)$ Å, $\beta = 92.024(6)^\circ$, $V = 2280.7(14)$ Å^3, $Z = 4$.

Keywords: Rheological phase synthesis; Diphosphonate; Antiferromagnetic

1. Introduction

Recent progress in the design and construction of metal phosphonates has been driven by the need to understand the physical properties and their potential sensing, ion-exchange catalysis and magnetic properties [1]. Among the diversity of metal phosphonate compounds, diphosphonic acids [$(HO)_2OPRPO(OH)_2$, where R is an organic group] and phosphonic acids [$ROP(OH)_2$] are excellent precursors for the preparation of such hybrid materials [2]. Many metal diphosphonate compounds have been prepared, most structurally determined either by single-crystal diffraction techniques or from X-ray powder diffraction data.

In these compounds, coordination geometries can be controlled with predictable topology and dimensions; metals can be pre-selected to impart functional properties, such as luminescence and magnetism [3]; multifunctional organic groups can be modified by other functional groups such as amino, hydroxy, pyridyl and carboxylate [4] to yield one- to three-dimensional structures. Further modification can be accomplished by changing the reaction conditions, length and structure of diphosphonic tether R or by introducing different templates [5].

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Our interest mainly focuses on the synthesis and the magnetic properties of transition metal–organic polymers with new structural features from simple ligands under mild conditions (usually 80°C). In this article, a new metal diphosphonate compound $[Co(HEDPH_2)_2](4,4'\text{-bipyH}_2)\cdot H_2O$ ($HEDPH_4$ = 1-hydroxyethylidenediphosphonic acid, 4,4′-bipy = 4,4′-bipyridine) was synthesized by rheological phase synthesis method, which is first declared in our lab [6] and has been applied in the preparation of electronic [7], photoluminescent [8] and nanosized diluted magnetic materials [9]. The method is a process for preparing compounds or materials from a solid–liquid rheological mixture. First, the starting materials are fully mixed in a proper molar ratio. Then water was added to form a liquid–solid rheological body in which the solid particles and liquid substances were uniformly distributed. After further treatment, the product was obtained. The compound was characterized by elemental analyses (EA), IR and thermogravimetric analysis (TGA). Furthermore, the magnetic properties of **1** were investigated and weak antiferromagnetic interactions found.

2. Experimental section

2.1. *Materials and measurements*

All the starting materials were purchased from commercial sources and used without further purification. IR spectra were recorded from KBr pellets from 400–4000 cm^{-1} on a Nicolet 5700 FTIR spectrometer with resolution of 4.00 cm^{-1}. Thermogravimetric studies were carried out with a NETZSCH STA 449C at a heating rate 20 K min^{-1} under air. The X-ray diffraction (XRD) patterns were obtained by Shimadzu XRD-6000 diffractometer with a Ni filter and Cu-Kα_1 radiation ($\lambda = 1.54056$ Å). The elemental analyses were obtained from a PERKIN-Elmer 240B.

2.2. *Synthesis of compound 1*

In a typical synthesis, to get a rheological phase, 0.0623 g (0.25 mmol) $Co(CH_3COO)_2\cdot 2H_2O$, 0.1838 g (0.5 mmol) 50% aqueous solution of $HEDPH_4$, 0.0390 g (0.25 mmol) 4,4′-bipy and 0.5 mL H_2O were mixed in 15 mL Teflon-lined stainless steel vessel. After reaction at 80°C for 2 days, pink block-shaped crystals were obtained in 80% yield. Elemental analyses for **1**: $C_{14}H_{24}N_2O_{15}P_4Co$: (Mr = 643.16). Anal. Calcd (%): N, 4.36; C, 26.14; H, 3.76. Found (%): N, 4.30; C, 26.23; H, 3.83.

2.3. *X-ray crystallography*

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer and performed at room temperature (293 K) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for absorption using the program SADABS. The structures were solved by direct methods using SHELXS-97 [10]. H1W1, H2W1, H11, H16, H17 and H22 were located in a difference map and refined isotropically. The other H atoms were placed in idealized

Table 1. Crystallographic data and structure refinement for compound **1**.

Empirical formula	$C_{14}H_{24}N_2O_{15}P_4Co$
Formula weight	643.16
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	15.754(6)
b (Å)	14.457(5)
c (Å)	10.020(4)
β (°)	92.024(6)
Volume (Å^3)	2280.7(14)
Z	4
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.10$
Data completeness	0.974
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0562$, $wR_2 = 0.1444$
R indices (all data)	$R_1 = 0.0627$, $wR_2 = 0.1552$

(a)$R_1 = [\Sigma(|F_o| - |F_o|)/\Sigma|F_o|$; (b)$wR_2 = [\Sigma[w(|F_o|^2 - |F_o|^2)^2]/\Sigma[w(|F_o|^2)^2]]^{1/2}, w = 1/[\sigma^2|F_o|^2 + (xp)^2 + yp]$; where $p = [|F_o|^2 + 2|F_0|^2]/3$.

Table 2. Selective bond lengths (Å) and angles (°) for **1**.

Co(1)–O(7)	2.019(4)	Co(1)–O(10)^{ii}	2.122(3)
Co(1)–O(8)	2.105(3)	P(1)–O(3)	1.489(3)
Co(1)–O(3)^{i}	2.106(3)	P(1)–O(1)	1.506(3)
Co(1)–O(1)	2.120(4)	P(1)–O(2)	1.571(4)
O(7)–Co(1)–O(12)	84.15(14)	O(8)–Co(1)–O(3)^{i}	88.10(14)
O(7)–Co(1)–O(8)	171.19(14)	O(7)–Co(1)–O(1)	91.87(14)
O(12)–Co(1)–O(8)	89.68(15)	O(12)–Co(1)–O(1)	171.43(13)
O(7)–Co(1)–O(3)^{i}	86.63(14)	O(8)–Co(1)–O(1)	95.06(13)
O(12)–Co(1)–O(3)^{i}	98.68(14)	O(7)–Co(1)–O(1)	91.87(14)
O(3)^{i}–Co(1)–O(1)	88.62(14)		

Symmetry codes: (i) $x, -y+2, z+1/2$; (ii) $x, -y+2, z-1/2$.

locations, with C–H = 0.95 Å, N–H = 0.86 Å, O–H = 0.82 Å and refined using a riding model; for all H atoms, $U_{iso}(H) = 1.2\,U_{eq}(C, N, O)$. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97. Figures were produced with PLATON [11]. A summary of crystallographic data for this compound is listed in table 1. More details are given in the supporting information.

3. Results and discussion

3.1. *Synthesis*

The compound was prepared by rheological phase synthesis at mild conditions (80°C). The core of this method is a rheological phase system, in which the surface area of the solid particles can be utilized efficiently due to the close and uniform contact between solid particles and fluid. During the experiment, we found that (4,4′-bipy) was necessary for the synthesis. The final products were not sensitive to the molar ratio of metal ion, diphosphonic acid and second ligand. In spite of the molar ratio of the starting materials as 1 : 2 : 1, 1 : 2 : 2 or 1 : 2 : 3, single crystals with the same structure were obtained; all were characterized by XRD (see S-1 in supporting information).

3.2. *Crystal structure*

Compound **1** crystallizes in space group *Cc* containing $[Co(HEDPH_2)_2]_n^{2n-}$ as an anionic chain, a 4,4′-bipyH_2^{2+} counter ion and a lattice water. Figure 1 shows cobalt(II) adopts a distorted octahedral coordination geometry with O–Co–O bond angles ranging from 84.08(13) to 172.48(15)°. The Co(1)–O bond lengths fall between 2.019(4) and 2.122(3) Å. These values are close to those of $[NH_3(CH_2)_4NH_3]Co_2(HEDPH)\cdot 2H_2O$ and $[NH_3(CH_2)_5NH_3]Co_2(HEDPH)\cdot 2H_2O$ [12]. The $HEDPH_2^{2-}$ group functions as a tridentate, chelating bridging ligand using three of its six phosphonate oxygens, O(1), O(3), and O(7). The P–O(H) distances [1.558(3), 1.571(4) Å] are significantly longer than those of P–O and P–O(Co) [1.489(3)–1.506(3) Å], which are defined as P=O bonds. More details of bond distances and angles are given in table 2. The remaining, [O(6)], is pendant, and involved in the intra-molecule hydrogen bonding network (table 3). Two of the remaining three phosphonate oxygens are deprotonated.

Each $HEDPH_2^{2-}$ ligand adopts the same coordination, chelating and bridging cobalt into an infinite single chain along the *c*-axis (figure 2). Each coordinated $HEDPH_2^{2-}$ ligand donates a strong hydrogen bond to the other phosphonate oxygen atom from the

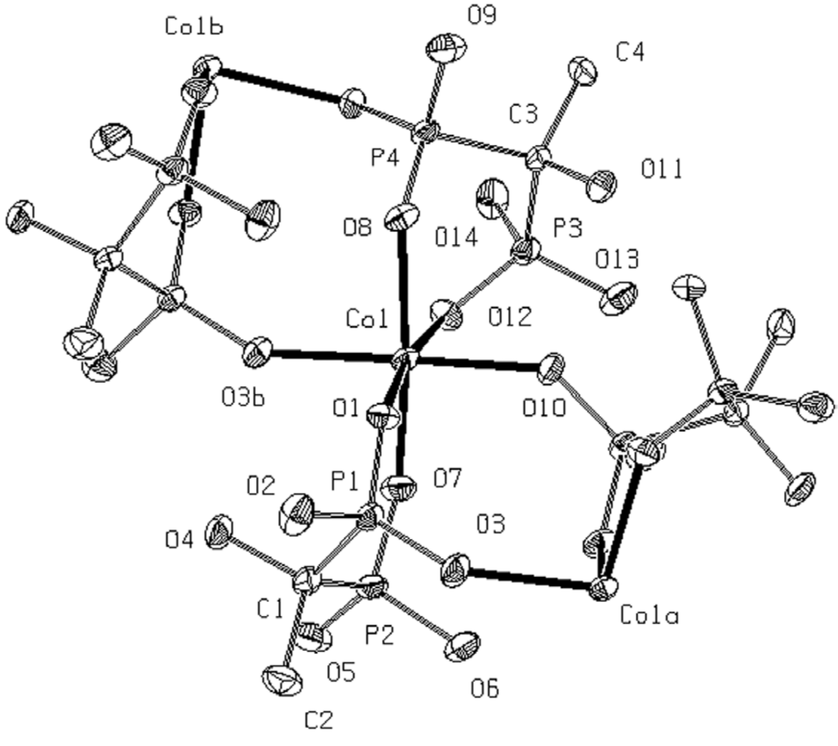

Figure 1. The coordination spheres around Co (50% probability) in **1**. All H atoms, 4,4′-bipyH_2^{2+} and H_2O are omitted for clarity.

Table 3. Hydrogen bonds for **1** (Å and °).

D–H···A	D···A	⟨D–H···A	D–H···A	D···A	⟨D-H···A
O(11)–H(18)···O(8)	2.923(5)	110.5	O(1W)–H(2W1)···O(9)^{iv}	2.974(6)	119(7)
O(2)–H(11)···O(1W)^{i}	2.600(7)	165(9)	O(1W)–H(2W1)···O(11)^{iv}	3.158(7)	161(8)
O(4)–H(12)···O(3)^{i}	2.823(5)	171.7	N(1)–H(1)···O(7)	2.836(7)	115.4
O(6)–H(16)···O(8)^{ii}	2.620(5)	176(8)	N(1)–H(1)···O(12)	2.687(7)	160.4
O(14)–H(22)···(5)^{v}	2.484(5)	160(8)	N(2)–H(6)···O(1)^{iii}	2.620(6)	166.0
O(11)–H(18)···O(10)^{ii}	2.730(5)	151.8			

Symmetry codes: (i) $x, -y+2, z+1/2$; (ii) $x, -y+2, z-1/2$; (iii) $x+1/2, -y+3/2, z+1/2$; (iv) $x-1/2$, y $-$ 1/2, z; (v) $x, y-1, z$.

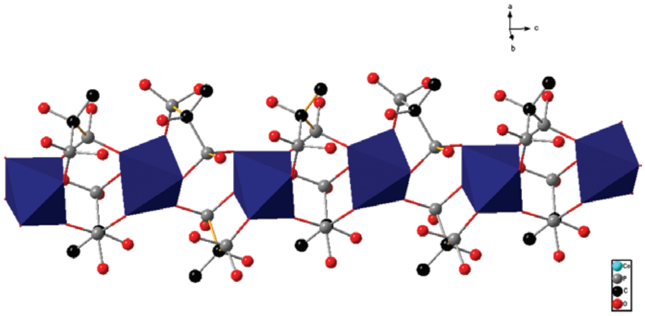

Figure 2. Fragment of the 1D Co–O–P–O–Co chain in compound 1. Should be replaced by A 1D chain structure in compound 1 along c-axis. The dark blue polyhedron represents a CdO6 unit. Hydrogen atoms are omitted for clarity.

neighboring chain [O(14)–H(22)···O(5)^{v}] (symmetry code: $v = x, -y+2, z+1/2$), and such supramolecular interactions extend the 1-D chains into a three-dimensional architecture, generating channels along the *c*-axis (figure 3a). Lattice water enhances this framework. As shown in figure 3(b), the protonated 4,4′-bipy is encapsulated in this channel and hydrogen-bonded to the phosphonate oxygen atoms through the strong N–H···O bonds, the average bond length is 2.714 Å.

3.3. *IR spectra, thermal analysis and XRD*

As shown in figure 4, IR spectra of **1** display broad bands centered at 3414 cm^{-1}, assigned to the OH stretching vibrations. The broadness is indicative of hydrogen bonds and in accord with the crystal structure. **1** has a series of three strong bands in the 920–1140 cm^{-1} range associated with ν (P–O) of the diphosphonate ligands. The bands at 1597m, 1475w and 1446m cm^{-1} can be assigned to the stretching bands of the pyridyl rings of 4,4′-bipy ligands [4d].

Thermogravimetric analysis (TGA) is carried out to examine the thermal stability of **1**. The TGA curve (figure 5) shows that **1** is stable in air to 158°C. The first loss of water occurs between 158 and 200°C. The weight loss is 3.0% and close to the calculated value 2.8%. The second step is related to partial removal of protonated 4,4′-bipy from 200 to 350°C (19.02%), total 4,4′-bipy removal was complete at 450°C (Calcd 23.94%). The TGA and DTG curves show the removal of protonated 4,4′-bipy

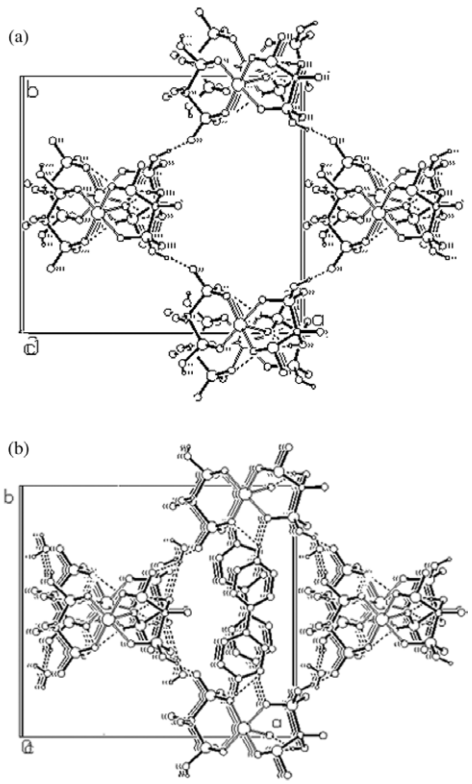

Figure 3. (a) Four neighboring chains are assembled via hydrogen bonds into a 3-D supramolecular structure with channels. (b) The protonated 4,4′-bipyH_2^{2+} molecules are encapsulated in the channels.

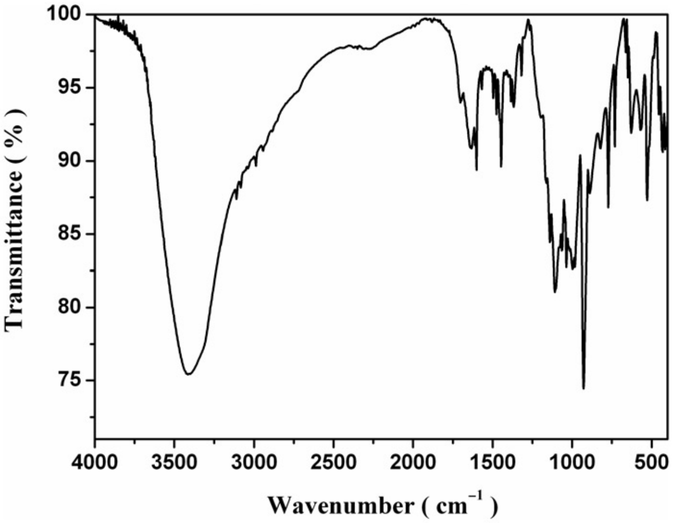

Figure 4. IR-spectra for **1**.

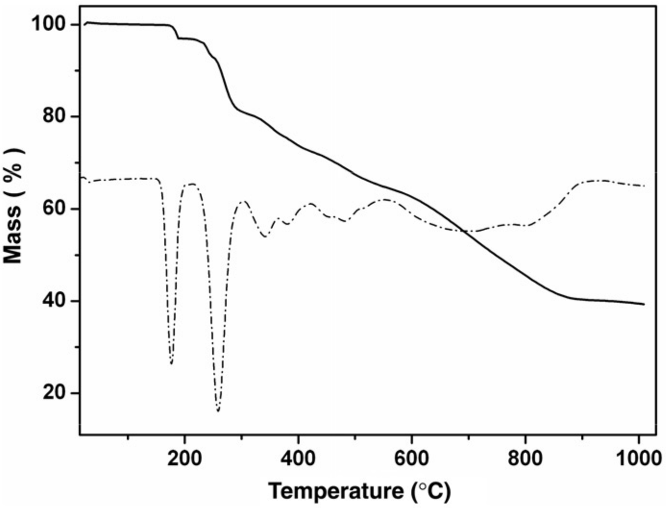

Figure 5. TGA/DTG curves for **1**.

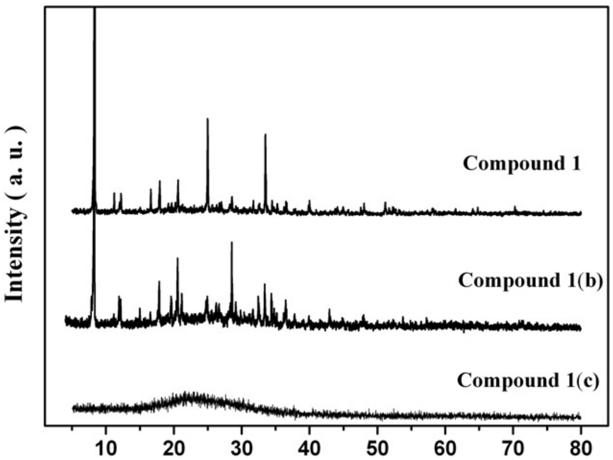

Figure 6. X-ray diffraction patterns of compound **1**, **1(b)** and **1(c)**.

step by step. The weight loss between 450 and 1000°C corresponds to decomposition of $HEDPH_2$. The final products are not characterized.

Calcination of **1** was carried out in air at 200°C for 12 h, resulting in calcined **1**(b). Although crystal **1**(b) is not sufficient for single-crystal diffraction, it is determined by powder XRD experiments. Figure 6 shows that the patterns of 1 and 1(b) are similar although the intensities and widths of some peaks show differences, indicating that the lattice water just enhances the 3-D supramolecular structure. Continuing calcination of compound **1**(b) is carried out in air at 350°C for 12 h, resulting in calcined **1**(c). The XRD pattern of **1**(c) show it becomes an amorphous phase, indicating that protonated 4,4′-bipy stabilize the channel structure, due to strong N–H···O bonds. The decomposition of diprotonated 4,4′-bipy results in the collapse of the framework.

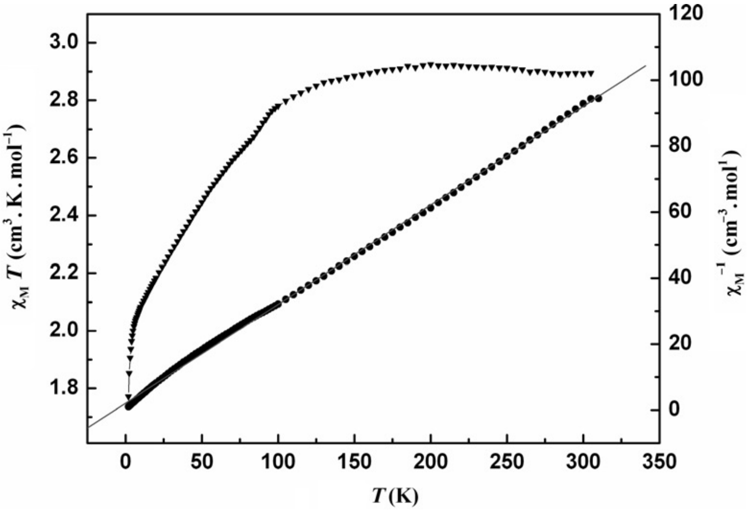

Figure 7. $\chi_M T$ and $\chi_M{}^{-1}$ *vs.* T plots for **1**.

3.4. *Magnetic properties*

The magnetic properties of **1** were investigated in the temperature range of 2–300 K. The effective magnetic moment per Co at 300 K is 4.81 μ_B higher than the spin only value for $S = 3/2$ centers (3.87 μ_B), indicating significant orbital contribution of Co(II). As shown in Figure 7, on cooling from room temperature, the $\chi_M T$ value decreases continuously indicating weak antiferromagnetic interactions between the Co(II) centers, confirmed by a negative Weiss constant ($\theta = -6.87$ K) determined by the Curie–Weiss law $\chi_M = C/(T - \theta)$. From the structure, the distance of adjacent Co ions is 5.100 Å over the O–P–O bridges. The weak antiferromagnetic interaction should be mainly attributed to the super exchange couplings between Co(II) centers through O–P–O bridges in the chain.

4. Conclusion

A new metal-diphosphonate compound has been synthesized by rheological phase reaction at 80°C. Single-crystal diffraction analysis shows it contains a 1-D chain structure, and hydrogen-bonding organization of 1-D chains into a 3-D supramolecular architecture. Furthermore, thermal stability and structure stability are characterized by TGA and XRD analysis. Weak antiferromagnetic interactions are found in the 1D Co–O–P–O–Co chain in compound **1**.

Supplementry material

Complete crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 294200. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam. ac.uk).

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