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Chiral Layered Zincophosphate $[d\text{-Co(en)}_3]\text{Zn}_3(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$ Assembled about $d\text{-Co(en)}_3{}^{3+}$ Complex Cations

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A new chiral layered zincophosphate $[d\text{-Co(en)}_3]\text{Zn}_3(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$, designated ZnPO-CJ16, has been hydrothermally synthesized by using the optically pure chiral metal complex $d\text{-Co(en)}_3\text{I}_3$ as the template. It contains 4.6-net sheets which array in a helical fashion with an ABCDEF stacking sequence along the [001] direction. The chiral $d\text{-Co(en)}_3{}^{3+}$ complex cations reside in the interlayer regions. Interestingly, there exist symmetrical O•••H•••O H-bonds between inorganic sheets, which results in a pseudo-three-dimensional open-framework structure stabilized by strong H-bonds. The crystal data are as follows: ZnPO-CJ16, $[d\text{-Co(en)}_3]\text{Zn}_3(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$; $M = 818.26$; hexagonal; $P6_522$ (No. 179); $a = 8.5832(12)$ Å; $c = 52.610(11)$ Å; $U = 3356.6(9)$ Å^3; $T = 293(2)$ K; $Z = 6$; $R_1 = 0.0415$ ($I > 2\sigma(I)$); $wR_2 = 0.1383$ (all data); Flack parameter, 0.04(4).

Introduction

The synthesis of chiral framework materials is of considerable interest, because of their promising applications in optical, enantioselective catalysis and separation.[1−6] One of the synthetic approaches to these materials is to incorporate chiral groups into organic−inorganic hybrid frameworks.[7] A notable example is the synthesis of robust chiral hybrid structure $[\text{Cd(QA)}_2]$ which can resolve racemic mixtures of small organic molecules.[7] Recently, Harrison and Gordon reported the synthesis of a zinc phosphite by using the L-asparagine as both the ligand and the template.[8] The other effective approach is to use chiral templates to impart their chirality into the open frameworks. The use of chiral metal complex templates has greatly facilitated the formation of chiral framework metal phosphates. Employing racemic or pure chiral metal complexes as the templates, a number of metal phosphates have been prepared.[9−14] Our research group has systemtically investigated the chirality transferrence from the guest chiral complex templates to the inorganic host frameworks.[15−21] Structural analysis reveals that hydrogen bonding between the guest metal complex and the host inorganic framework is the orgin of chiral transference.[17] By using a racemic mixture of chiral *trans*-

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$Co(dien)_2^{3+}$ complex cations as the template, an open-framework zinc phosphate [*trans*-$Co(dien)_2$]$Zn_2(HPO_4)_4$•H_3O with multidirectional helical channels was successfully synthesized.[16] It is believed that using a rigid optically pure chiral complex as a template will lead to the formation of chiral host frameworks. So far, only three examples are known as [*d*-$Co(en)_3$]$Al_3P_4O_{16}$•$2H_2O$,[12] [*d*-$Co(en)_3$]$H_3Ga_2P_4O_{16}$,[14] and [*d*-$Co(en)_3$]AlP_2O_8•$6.5H_2O$.[21]

In this work by using the optically pure chiral metal complex *d*-$Co(en)_3I_3$ as the template, a new chiral layered zincophosphate [*d*-$Co(en)_3$]$Zn_3(H_{0.5}PO_4)_2(HPO_4)_2$, designed ZnPO-CJ16, has been prepared under the hydrothermal condition. Notably, symmetrical O•••H•••O bonds, are observed in ZnPO-CJ16.

Experimental Section

Synthesis of ZnPO-CJ16. Large single crystals of ZnPO-CJ16 were prepared by a hydrothermal reaction of a mixture of $Zn(OAc)_2$•$2H_2O$, H_3PO_4, *d*-$Co(en)_3I_3$,[22] TMAOH (tetramethylammonium hydroxide 10 wt %), and H_2O in a molar ratio of 1.0:3.0:0.18:2.0:488.0. Typically, $Zn(OAc)_2$•$2H_2O$ (0.25 g) was first dissolved in H_2O (8 mL), and then H_3PO_4 (85 wt %, 0.231 mL) was added with stirring followed by the addition of *d*-$Co(en)_3I_3$ (0.127 g). Finally, TMAOH (2 mL) was added to the above reaction mixture. The resulting gel with a pH value of 4.0 was stirred for 1 h until it was homogeneous, then sealed in a Teflon lined stainless steel autoclave, and heated at 10 °C for 72 h under static conditions. The product containing orange hexagonal blocklike single crystals was separated by sonication, further washed by distilled water, and then air-dried.

Characterization. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer TGA 7 unit instrument was used to carry out the thermogravimetric analysis (TGA) in the air at a heating rate of 10 °C/min. The ^{31}P magic-angle spinning (MAS) NMR experiment was carried out on a solid-state NMR Infinity Plus 400 spectrometer equipped with a standard 4 mm MAS probe head at 9.4 T. The resonance frequency was 104.3 MHz. The chemical shift was referenced to 85% H_3PO_4 solutions.

Structural Determination. A suitable single crystal of ZnPO-CJ16 with dimensions of 0.2 × 0.2 × 0.15 mm was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program.[23] The structure was solved in the space group of $P6_522$ by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97.[24] The flack parameter was 0.04(4), confirming the determined absolute structure. It was noted that six randomly selected crystals were the same enantiomer in the space group of $P6_522$. All Zn, Co, P, O, C, and N atoms were easily located in the difference Fourier maps. H atoms attached to the metal complex cations were placed geometrically and refined using a riding model. The H atoms attached to the terminal oxygen atoms were found in the difference Fourier map, in which H(1) lies at the center of the O(1) and O(1A) atoms. All non-hydrogen atoms were refined anisotropically. Experimental details for the structural determination and selected bond distances and angles are presented in Tables 1 and 2, respectively.

Table 1. Crystal Data and Structural Refinement for ZnPO-CJ16

identification code	ZnPO-CJ16
empirical formula	$C_6H_{27}CoN_6O_{16}P_4Zn_3$
formula weight	818.26
temperature	293(2) K
wavelength	0.71073 Å
crystal system, space group	hexagonal, $P6_522$
unit cell dimensions	$a = 8.5832(12)$ Å
	$b = 8.5832(12)$ Å
	$c = 52.610(11)$ Å
volume	3356.6(9) Å^3
Z, calculated density	6, 2.429 Mg/m^3
absorption coefficient	4.282 mm^{-1}
$F(000)$	2460
crystal size	0.2 × 0.2 × 0.15 mm
theta range for data collection	2.32−23.25°
limiting indices	$-9 \leq h \leq 4$, $-9 \leq k \leq 9$, $-58 \leq l \leq 57$
reflections collected/unique	16098/1624 [$R_{int} = 0.0714$]
completeness to theta = 23.25	100.0%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1624/0/171
goodness of fit on F^2	1.032
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0415$, $wR_2 = 0.1354$
R indices (all data)	$R_1 = 0.0448$, $wR_2 = 0.1383$
absolute structure parameter	0.04(4)
extinction coefficient	0.0010(3)
largest diff. peak and hole	0.624 and −0.488 e•Å^{-3}

Table 2. Bond Lengths [Å] and Angles [deg] for ZnPO-CJ16

Zn(1)−O(2)	1.941(7)	Zn(1)−O(6)	1.970(6)
Zn(2)−O(3)	1.908(6)	Zn(2)−O(7)	1.915(7)
Zn(2)−O(8)^a	1.944(7)	Zn(2)−O(5)	1.973(7)
P(1)−O(2)	1.494(7)	P(1)−O(8)	1.530(7)
P(1)−O(7)^b	1.536(7)	P(1)−O(1)	1.552(6)
P(2)−O(3)^c	1.509(7)	P(2)−O(5)	1.525(7)
P(2)−O(6)	1.519(7)	P(2)−O(4)	1.604(6)
O(1)−H(1)	1.234(6)	O(4)−H(4)	0.91(11)
P(1)−O(1)−H(1)	116.3(7)	P(1)−O(2)−Zn(1)	137.0(4)
P(2)^d−O(3)−Zn(2)	139.8(4)	P(2)−O(4)−H(4)	107(7)
P(2)−O(5)−Zn(2)	131.0(4)	P(2)−O(6)−Zn(1)	126.8(4)
P(1)^e−O(7)−Zn(2)	131.7(4)	P(1)−O(8)−Zn(2)^f	140.2(5)

$^{a-f}$ Symmetry transformations used to generate equivalent atoms: (a) $x - y - 1, -y, -z$; (b) $x + 1, y, z$; (c) $x - y + 1, -y + 1, -z$; (d) $x - y, -y + 1, -z$; (e) $x - 1, y, z$; and (f) $x - y + 1, -y, -z$.

Result and Discussion

Figure 1 shows that the experimental XRD pattern for ZnPO-CJ16 is in accord with the simulated one generated on the basis of structural data except for some intensity difference, which may be due to the preferred orientation of the crystals. This confirms that the as-synthesized product is a pure phase.

The determined ICP data of ZnPO-CJ16 (Zn, 24.48 wt %; P, 14.96 wt %; Co, 7.12 wt %) are in agreement with the calculated values (Zn, 23.97 wt %; P, 15.14 wt %; Co, 7.20 wt %). The determined C, H, and N data of ZnPO-CJ16 (C, 8.81 wt %; H, 3.05 wt %; N, 10.30 wt %) are in agreement with the calculated values (C, 8.81 wt %; H, 3.33 wt %; N, 10.27 wt %).

Figure 2 shows the TG curve of ZnPO-CJ16. Major weight loss of 18.36% (calcd, 22.41%) occurring at 200−

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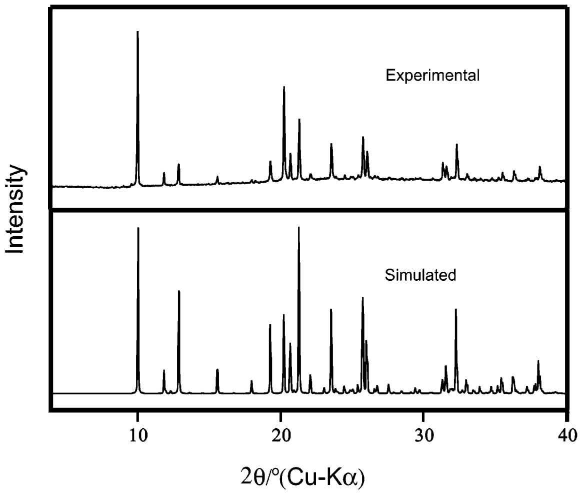

Figure 1. Experimental and simulated XRD patterns for ZnPO-CJ16.

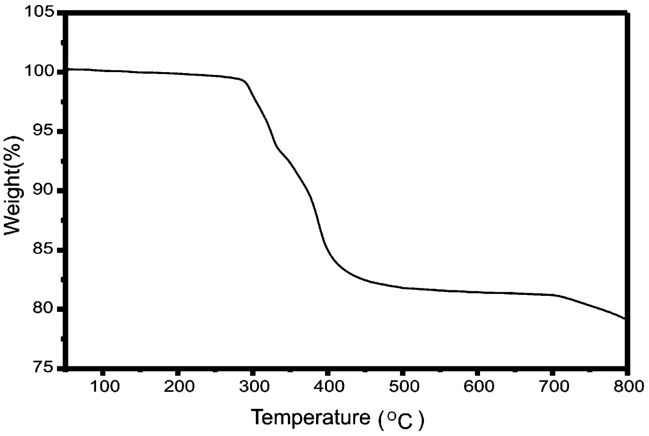

Figure 2. TG curve of ZnPO-CJ16.

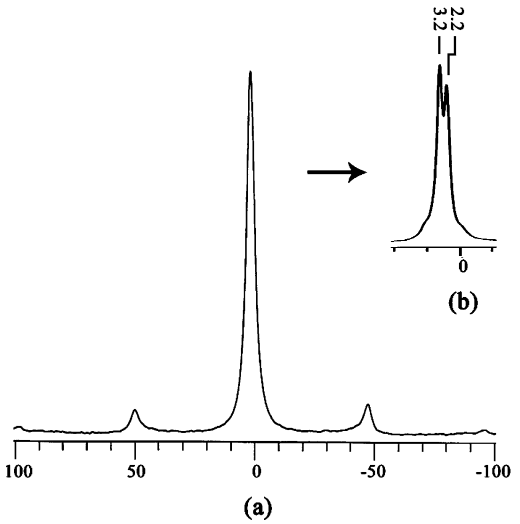

Figure 3. (a) ^{31}P MAS NMR spectrum of ZnPO-CJ16 without ^{1}H decoupling; (b) ^{31}P MAS NMR with ^{1}H decoupling spectrum of ZnPO-CJ16.

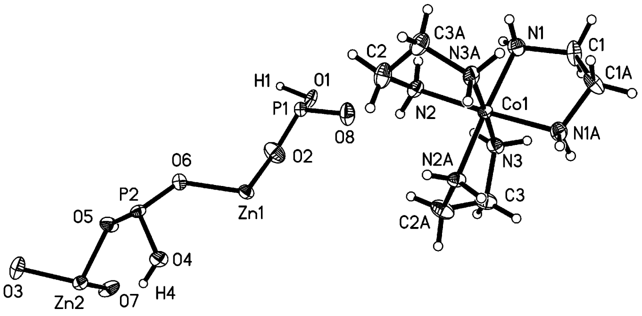

Figure 4. Thermal ellipsoid plot (50%), showing the asymmetric unit of ZnPO-CJ16.

550 °C was observed, which is due to the decomposition of the metal complex. Minor weight loss of 3.14% (calcd, 3.30%) in the range of 550−800 °C corresponds to the dehydration of the HPO_4 and $H_{0.5}PO_4$ groups corresponding to $1.5H_2O$ per formula.

One resonance with an isotropic chemical shift at around 3.0 ppm is observed in the ^{31}P MAS NMR spectrum (Figure 3a) that indicates the tetrahedral coordination of P atoms. The ^{31}P MAS NMR with the ^{1}H decoupling spectrum of ZnPO-CJ16 (Figure 3b) shows two resonances at 2.2 and 3.2 ppm, respectively, and their relative intensities are very close to 1:1. These correspond to two crystallographically distinct P sites, HPO_4 and $H_{0.5}PO_4$. It further confirms the different environments of P atoms affected by the vicinal effect of H atoms.

The structure of ZnPO-CJ16 consists of chiral macroanionic $[Zn_3(H_{0.5}PO_4)_2(HPO_4)_2]^{3-}$ sheets. Charge neutrality of the framework is achieved by the *d*-$Co(en)_3^{3+}$ complex cations residing in the interlayer regions. The asymmetric unit, as seen in Figure 4, contains two crystallographically distinct Zn atoms and two crystallographically distinct P atoms. The Zn atoms are tetrahedrally coordinated with oxygen atoms, sharing four vertex oxygen atoms with adjacent P atoms. Zn(1) is located at a special position with C_2 symmetry, and Zn(2) is located at a general position. The Zn−O distances are in the range of 1.908(6)−1.973(7) Å, and the O−Zn−O angles are in the range of 99.1(3)−123.0(3)°, which are typical values for zinc phosphates.[15−17] Two distinct P atoms are both tetrahedrally coordinated with oxygen atoms, sharing three oxygen atoms with adjacent Zn atoms, leaving one terminal $OH/OH_{0.5}$ group. The $P-O_{bridging}$ distances are in the range of 1.494(7)−1.536(7) Å, and the longer P−OH distances are 1.552(6) and 1.604(6) Å. The crystallographically distinct Co atom lies on the twofold axis.

The structure of ZnPO-CJ16 is built up from strictly alternating ZnO_4 and $PO_3OH/PO_3OH_{0.5}$ tetrahedral units that are linked through their vertexes, giving rise to the two-dimensional layered structure with 4.6 nets. Figure 5 shows that the inorganic sheet contains a series of [3.3.3] propellane-like chiral structural motifs with C_2 symmetry. This chiral motif has been observed in a number of metal phosphate templated by racemic or chiral metal complex.[9−12,15,19,20] Moreover, the symmetry and configuration of the chiral inorganic motif confirms those of the chiral complex template, revealing a stereospecific correspondence between the guest chiral complex template and the host inorganic framework.[17] Interestingly, the 4.6-net sheets of the ZnPO-CJ16 array in a helical fashion with ABCDEF stacking sequences along the 6_5 screw axis as shown in Figure 6. It is noted that the structure of ZnPO-CJ16 is analogous to that of the layered aluminophosphate [*trans*-$Co(dien)_2]Al_3P_4O_{16}\cdot 3H_2O$

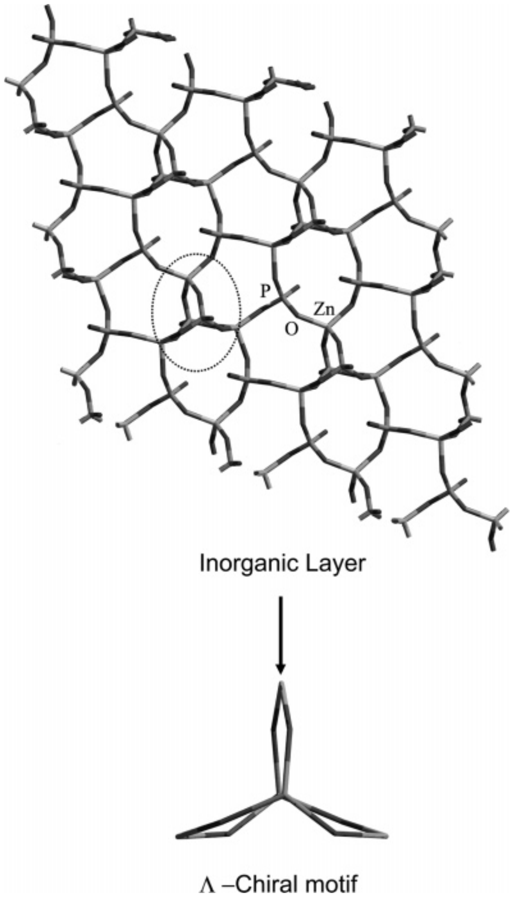

Figure 5. 4.6-net sheet structure of ZnPO-CJ16 parallel to the *ab* plane.

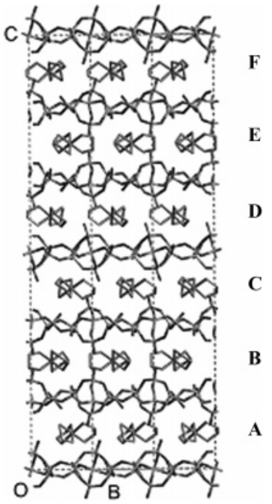

Figure 6. Packing of 4.6-net sheets of ZnPO-CJ16 in an ABCDEF stacking sequence along the 6_5 screw axis, with *d*-Co(en)$_3^{3+}$ cations in the interlayer regions. H atoms are omitted for clarity.

templated by *trans*-Co(dien)$_2^{3+}$ cations.[11] However, the interlayer distances in these two compounds differ greatly (ZnPO-CJ16: 8.77 Å; [*trans*-Co(dien)$_2$][Al$_3$P$_4$O$_{16}$]$\cdot$3H$_2$O: 10.55 Å). The shorter interlayer distance of ZnPO-CJ16 may be caused by the strong symmetrical O···H···O H-bonds between the adjacent layers.

Table 3. Hydrogen Bonds and Angles for ZnPO-CJ16 [Å and deg]

D−H···A	*d*(H···A)	*d*(D···A)	<(DHA)
O(4)−H(4)···O(8)^a	1.80	2.691(10)	166
N(1)−H(1C)···O(6)^b	2.12	2.992(10)	163
N(2)−H(2C)···O(4)^c	2.46	2.988(9)	118
N(3)−H(3C)···O(5)^b	1.88	2.783(10)	176
N(3)−H(3D)···O(1)^d	2.19	2.969(10)	145

$^{a-d}$ Symmetry transformations used to generate equivalent atoms: (a) $x - y - 1, -y, -z$; (b) $x - y + 1, -y, -z$; (c) $x + 1, y, z$; and (d) $x - y, -y - 1, -z$.

Symmetrical H-bonds with an O···O distance < 2.5 Å found in hydrates/ice,[25] carboxylic acid−carboxylates,[26] enols,[27] and so on[28] are rarely observed in the metal phosphates. As far as we have known, only one reported gallophosphate has this unique character.[29] In its structure, the H atom lying on an inversion center is shared by two PO$_4$ groups of adjacent chains to form strong symmetrical H-bonds with an O···O distance of 2.46 Å. In the structure of ZnPO-CJ16, the H(1) atom lying on the midpoint of O(1) and O(1A) atoms can be located easily from the Fourier map. Thus, the symmetrical H-bonds are formed between inorganic sheets with an O(1)···O(1A) distance of 2.468 Å (Figure 6), which is consistent with the reported data.[28a,d−g] Moreover, the study of Paola et al. shows that when the O···O distance is shortened from 2.8 to 2.4 Å, the H-bond is transformed from a dissymmetrical O−H···O electrostatic interaction to a covalent and symmetrical O···H···O bond.[28b] Herein, a pseudo-three-dimensional structure is formed by the H(1) atom together with the adjacent layers. It contains two pseudo-12-ring channels along the [100] and [010] directions, respectively, and a *d*-Co(en)$_3^{3+}$ complex cation resides in each pseudo-12-MR window to form extensive H-bonds with the lattice oxygen atoms; the N···O distances are in the range of 2.783(10)−2.992(10) Å, as shown in Table 3.

ZnPO-CJ16 exhibits a new type of layered structure in the zinc phosphate family, and it is the first zincophosphate structure templated by a pure chiral metal complex. So far, only a few examples of metal phosphates are known to be templated by an optically pure chiral template.[12,14,21] The absolute structure determination demonstrates that the ex-

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amined crystal contains only one enantiomer of *d*-$Co(en)_3^{3+}$ complex cations. The optical rotation measurement is used to characterize the chirality of the as-synthesized product. The solution of the as-synthesized product dissolved in the HNO_3 solution shows optical rotation. Furthermore, [*l*-$Co(en)_3]Zn_3(H_{0.5}PO_4)_2(HPO_4)_2$ with the space group of $P6_122$ is also prepared by using optically pure *l*-$Co(en)_3I_3$ as the template under similar conditions. XRD analysis shows that its structure is analogous to that of [*d*-$Co(en)_3]Zn_3(H_{0.5}PO_4)_2(HPO_4)_2$ with the space group of $P6_522$, and similar optical activity is observed. Even though it is difficult to perform quantitative measurements of optical activity of the product, the above results indicate that no significant racemization of *d*-$Co(en)_3^{3+}$ or *l*-$Co(en)_3^{3+}$ ions occurs under our synthesis conditions. Otherwise, the reaction gel will contain a mixture of *d*- and *l*-$Co(en)_3^{3+}$ cations, which leads to the formation of [*d*,*l*-$Co(en)_3]_2[Zn_6P_8O_{32}H_8]$[15] rather than a mixture of [*d*-$Co(en)_3]Zn_3(H_{0.5}PO_4)_2(HPO_4)_2$ and [*l*-$Co(en)_3]Zn_3(H_{0.5}PO_4)_2(HPO_4)_2$. However, it might be unavoidable that trace of chiral templates *d*-$Co(en)_3^{3+}$ or *l*-$Co(en)_3^{3+}$ racemize or decomposite.[21]

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Supporting Information Available: Crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. This material also available at http://www/rsc.org/ from the CCDC (reference number 250548).

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