$[C_2N_2H_{10}]_{1.5}[Nd(SO_4)_3(H_2O)] \cdot 2H_2O$: The first organically templated neodymium sulfate with a layer structure

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Abstract

The first organically templated neodymium sulfate has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction analysis. $[C_2N_2H_{10}]_{1.5}[Nd(SO_4)_3(H_2O)] \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with crystal data $a = 6.5896(5)$ Å, $b = 26.539(3)$ Å, $c = 9.9889(8)$ Å, $\beta = 104.399(5)°$, $V = 1692.0(2)$ Å^3, $Z = 4$. Refinement gave $R_1[I > 2\sigma(I)] = 0.0471$, and $wR_2[I > 2\sigma(I)] = 0.0899$. The compound exhibits an infinite zigzag anionic layer structure, which consists of $\{Nd(SO_4)_3(H_2O)\}^{3-}$ structural units connected together to form interesting eight-membered rings via corner-sharing and edge-sharing modes. The compound has the antiferromagnetic behavior and exhibits intense photoluminescence upon photo-excitation at 450 nm.

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Keywords: Hydrothermal synthesis; Inorganic microporous material; Fluorescent property; Magnetic property; Layer; Neodymium sulfate; Crystal structure

1. Introduction

A remarkable variety of organically templated open-framework inorganic microporous materials have been synthesized over the last decades, due to their rich structure chemistry and potential applications in catalysis, separation and ion-exchange [1,2]. In these materials, most of them are silicates [3] and phosphates [4], there also have been great efforts to synthesize other compounds with open-framework structures, such as, arsenates [5,6], phosphites [7,8], selenites [9,10] and germanates [11,12]. Recently, considerable interest has been grown in the study of organically templated open-framework metal sulfates. Rao et al. reported the first members of the family of cadmium sulfates in the presence of organic amines or directly with amine sulfates under mild hydrothermal conditions [13,14]. Up to now, other metal sulfates have been hydrother-

mally synthesized. They are lanthanide sulfates [15–17], uranium sulfates [18,19], iron sulfate [20] and nickel sulfate [21], etc.

Owing to the high coordination numbers (from 7- to 12-fold), a variety of coordination geometries and the existence of changeable oxidation states of lanthanide elements, the syntheses of novel amine-based lanthanide materials are very important. In our group, we have successfully hydrothermally synthesized two lanthanide sulfate compounds [16,17]. Although neodymium belongs to the lanthanide elements, to our knowledge, no open-framework neodymium sulfates templated by organic amines have been reported hitherto. Here, we report the first neodymium sulfate compound $[C_2N_2H_{10}]_{1.5}[Nd(SO_4)_3(H_2O)] \cdot 2H_2O$ in the presence of ethylenediamine (en) as structure-directing agent. The as-synthesized product is characterized by means of powder X-ray diffraction, IR spectroscopy, fluorescent spectroscopy, inductive couple plasma analysis, thermogravimetric analysis, magnetic properties analysis and single crystal structure analysis.

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2. Experimental

2.1. Physical measurements

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The step size was $0.02°$ and the count time was 4 s. The elemental analyses were performed on a Perkin-Elmer 2400 Element Analyzer. The inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The infrared (IR) spectra were recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermal gravimetric analyses (TGA) and differential thermal analyses (DTA) were performed on Perkin-Elmer TGA 7 instrument and a Perkin-Elmer DTA 1700 differential thermal analyzer used in an atmospheric environment with a heating rate of 10 °C min^{-1}. Fluorescent spectrum was measured on a Perkin-Elmer LS 55 luminescence spectrometer, equipped with a 450 W xenon lamp. Variable-temperature magnetic susceptibility measurements were carried out in the 2–300 K range using a Quantum Design MPMS-7 SQUID magnetometer at a magnetic field of 5000G.

2.2. Synthesis

All reagents were purchased commercially and used without further purification. The title compound was hydrothermally synthesized under autogenous pressure. In a typical synthesis, solution I was prepared by dissolving 0.34 g of Nd_2O_3 into 10.0 mL diluted sulfuric acid (1 mL H_2SO_4/10.0 mL H_2O) under constant stirring. A total of 0.12 mL en was added to 10.0 mL diluted sulfuric acid (0.3 mL H_2SO_4/10.0 mL H_2O) under stirring to make solution II. Then solution I was mixed with solution II under constant stirring. The resulting mixture with a molar ratio of 1.0 Nd_2O_3:24.4 H_2SO_4:3.0 en:1100 H_2O was transferred into a 30 mL Teflon-lined autoclave and heated at 373 K for 2 days. The light purple block-like single crystals were isolated by filtration, washed with water, and dried in air at ambient temperature.

2.3. X-ray crystallography

A suitable single crystal ($0.32 \times 0.27 \times 0.26$ mm) was selected and mounted on a thin glass fiber by using cyanoacrylate. The intensity data were collected on a Rigaku RAXIS-RAPID diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at a temperature of 298 ± 2 K. The numbers of collected reflections and independent reflections were 12195 and 4210, respectively. Data processing was accomplished with the RAPID AUTO processing program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 [22]. The neodymium and sulfur atoms were first located and the carbon, nitrogen, oxygen atoms were found in difference Fourier maps. The hydrogen atoms of the amine molecule were placed geometrically. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Characterization

The ICP analyses indicate that the product contains 25.13 wt% of Nd and 16.22 wt% of S, in good agreement with the calculated values (24.84 wt% of Nd, 16.59 wt% of S). The element analyses show that the C, H, and N contents are 6.27, 3.58, and 7.22 wt%, respectively, corresponding to an empirical molar ratio of C:H:N = 6.21:3.62:7.24. These correspond well to a formula of $C_3H_{21}N_3NdO_{15}S_3$, which are further confirmed by single-crystal structure analysis.

The IR spectrum of the compound shows that the band at 3500 cm^{-1} is due to the presence of water. The typical sharp peaks for ethylenediamine are in the region 1340–1612 cm^{-1}, and characteristic bands due to the sulfate ion are in the 1091 and 611 cm^{-1} regions. Absorption at 784 cm^{-1} can be attributed to Nd–O vibration. The bands at 3010 and 3176 cm^{-1} are due to N–H bonding and O–H bonding vibrations, respectively.

The TG curve of the title compound shows that the weight loss is 9.06% from 100 to 300 °C, corresponding to the loss of the structural and coordinated water molecules (calc. 9.3%). There are two periods of sharp weight loss in the range 300–800 °C (obs. = 51.33%, calc. = 51.93%) due to the loss of amine molecules and SO_3. The whole weight loss (60.39%) is in agreement with the calculated value (61.23%). The sample does not lose weight at temperature higher than 800 °C. The powder X-ray diffraction pattern of the sample heated at 800 °C corresponds to $Nd_2O_2(SO_4)$ (JCPDS file card No. 23-1262), indicating destruction of the framework structure upon loss of the amine.

3.2. Crystal structure

The crystallographic data are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

The structure of the compound consists of inorganic anionic framework $\{Nd(SO_4)_3(H_2O)\}_n^{3n-}$, free water molecules and charge-compensated by the ethylenediamine cations located in accessible voids. The asymmetric unit is shown in Fig. 1. There are one crystallographi-

Table 1
Crystal data and structure refinement for the compound [$C_2N_2H_{10}$]$_{1.5}$[Nd(SO$_4$)$_3$(H$_2$O)] · 2H$_2$O

Empirical formula	C3 H21 N3 Nd O15 S3
Formula weight	579.65
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	6.5896(5)
b (Å)	26.539(3)
c (Å)	9.9889(8)
β (°)	104.399(5)
V (Å^3)	1692.0(2)
Z	4
Calculated density (Mg m^{-3})	2.275
Absorption coefficient (mm^{-1})	3.520
θ range for data collection (°)	1.53–28.38
Crystal size (mm)	0.32 × 0.27 × 0.26
Completeness to $\theta = 28.38$	99.2%
Reflections collected	12195
Reflections unique	4210
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0471$, $wR_2 = 0.0899$

Table 2
Selected bond lengths (Å) for the title compound

Nd(1)–O(5)	2.382(6)	S(2)–O(8)#2	1.475(7)
Nd(1)–O(6)	2.423(6)	S(2)–O(4)	1.484(6)
Nd(1)–O(9)	2.492(7)	S(2)–O(7)#2	1.489(6)
Nd(1)–O(3)	2.525(6)	S(2)–O(3)	1.490(6)
Nd(1)–O(1)	2.530(6)	S(3)–O(13)	1.460(7)
Nd(1)–O(2)	2.541(7)	S(3)–O(5)	1.476(7)
Nd(1)–O(7)	2.543(7)	S(3)–O(12)	1.483(7)
Nd(1)–O(8)	2.556(6)	S(3)–O(11)	1.486(7)
Nd(1)–O(4)	2.559(6)	N(1)–C(1)	1.486(13)
S(1)–O(10)	1.456(7)	N(2)–C(2)	1.472(13)
S(1)–O(6)#1	1.473(6)	N(3)–C(3)	1.511(14)
S(1)–O(1)	1.480(7)	C(1)–C(2)	1.526(14)
S(1)–O(2)	1.489(7)	C(3)–C(3)#3	1.46(2)

Symmetry transformations used to generate equivalent atoms: #1 $x-1,y,z$ #2 $x,-y+3/2,z+1/2$ #3 $-x+2,-y+1,-z$.

Table 3
Selected bond angles (deg) for the title compound

O(5)–Nd(1)–O(6)	80.7(2)	O(7)–Nd(1)–O(8)	55.2(2)
O(5)–Nd(1)–O(9)	76.4(2)	O(5)–Nd(1)–O(4)	78.5(2)
O(6)–Nd(1)–O(9)	80.6(2)	O(6)–Nd(1)–O(4)	72.2(2)
O(5)–Nd(1)–O(3)	87.8(2)	O(9)–Nd(1)–O(4)	145.4(2)
O(6)–Nd(1)–O(3)	127.5(2)	O(3)–Nd(1)–O(4)	55.39(19)
O(9)–Nd(1)–O(3)	145.3(2)	O(1)–Nd(1)–O(4)	118.6(2)
O(5)–Nd(1)–O(1)	129.5(2)	O(2)–Nd(1)–O(4)	122.3(2)
O(6)–Nd(1)–O(1)	148.1(2)	O(7)–Nd(1)–O(4)	71.1(2)
O(9)–Nd(1)–O(1)	95.7(2)	O(8)–Nd(1)–O(4)	122.8(2)
O(3)–Nd(1)–O(1)	70.8(2)	O(10)–S(1)–O(6)#1	111.3(4)
O(5)–Nd(1)–O(2)	75.0(2)	O(10)–S(1)–O(1)	110.9(4)
O(6)–Nd(1)–O(2)	147.5(2)	O(6)#1–S(1)–O(1)	110.0(4)
O(9)–Nd(1)–O(2)	73.1(2)	O(10)–S(1)–O(2)	110.3(5)
O(3)–Nd(1)–O(2)	73.1(2)	O(6)#1–S(1)–O(2)	109.2(4)
O(1)–Nd(1)–O(2)	55.4(2)	O(1)–S(1)–O(2)	105.0(4)
O(5)–Nd(1)–O(7)	146.6(2)	O(8)#2–S(2)–O(4)	112.1(4)
O(6)–Nd(1)–O(7)	77.1(2)	O(8)#2–S(2)–O(7)#2	105.8(4)
O(9)–Nd(1)–O(7)	123.3(2)	O(4)–S(2)–O(7)#2	111.5(4)
O(3)–Nd(1)–O(7)	86.3(2)	O(8)#2–S(2)–O(3)	111.0(4)
O(1)–Nd(1)–O(7)	78.8(2)	O(4)–S(2)–O(3)	105.2(4)
O(2)–Nd(1)–O(7)	133.6(2)	O(7)#2–S(2)–O(3)	111.2(4)
O(5)–Nd(1)–O(8)	141.9(2)	O(13)–S(3)–O(5)	109.0(4)
O(6)–Nd(1)–O(8)	77.7(2)	O(13)–S(3)–O(12)	110.6(4)
O(9)–Nd(1)–O(8)	69.4(2)	O(5)–S(3)–O(12)	109.1(4)
O(3)–Nd(1)–O(8)	130.2(2)	O(13)–S(3)–O(11)	111.1(4)
O(1)–Nd(1)–O(8)	71.5(2)	O(5)–S(3)–O(11)	108.6(4)
O(2)–Nd(1)–O(8)	109.2(2)	O(12)–S(3)–O(11)	108.3(4)

Symmetry transformations used to generate equivalent atoms: #1 $x-1,y,z$ #2 $x,-y+3/2,z+1/2$.
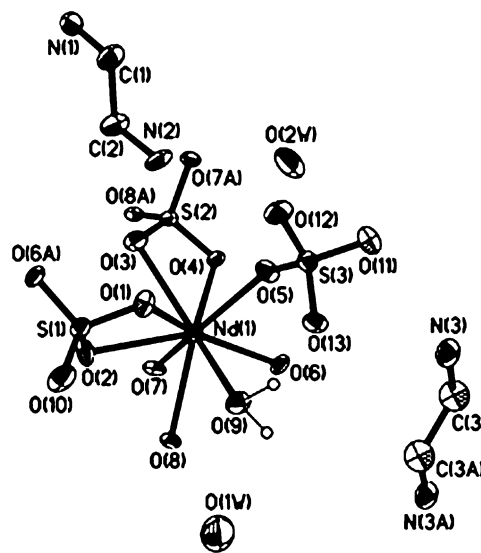

Fig. 1. ORTEP view of [$C_2N_2H_{10}$]$_{1.5}$[Nd(SO$_4$)$_3$(H$_2$O)] · 2H$_2$O structure showing the atom labeling scheme (50% thermal ellipsoids).

cally independent neodymium atom and three distinct sulfur atoms. The Nd atom is nine-fold coordinated by eight O atoms from five sulfate groups (2 × S$_1$, 2 × S$_2$, S$_3$) and one O atom from water ligand. The average value of Nd–O band length is 2.5063 Å. All three S atoms form the centers of tetrahedral sulfate groups. The S–O bond distances in the SO$_4$ tetrahedron are in the range of 1.456(7)–1.490(6) Å with an average value of 1.4791 Å. The O–S–O bond angles range from 105.0(4) to 112.1(4)°, which are close to the theoretical value of a tetrahedral angle. Of the three different S atoms, S(1) is tetrahedrally coordinated to four oxygen atoms, of which three share vertices and edges with two crystallographically unique Nd(1) atoms, the remaining is a terminal S = O group. The S(2)O$_4$ tetrahedron shares edges with two Nd(1)O$_9$ polyhedra neighbors.

The S(3) atom makes a S–O–Nd linkage to Nd(1) atom, O(11) and O(12) are "unsaturated" atoms, and O(13) is a terminal S = O group.

The inorganic layer can be viewed as being built up of {Nd(SO$_4$)$_3$(H$_2$O)}$^{3-}$ structural units constituted by

{NdO_9} polyhedra and {SO_4} tetrahedra. The linkage between the {Nd(SO_4)_3(H_2O)}^{3-} structural units results in a chain arrangement through bridging atom O(6) running along the *a*-axis. The chains are connected via two bridging atoms O(7) and O(8) from S(2)O_4 tetrahedra forming an infinite 2D layer in the *ac* plane. Within the layer, four such {Nd(SO_4)_3(H_2O)}^{3-} structural units are connected together to form an interesting eight-membered ring [–Nd(1)–S(2)–Nd(1)–S(1)–Nd(1)–S(2)–Nd(1)–S(1)–] via corner-sharing and edge-sharing modes, and S(3)O_4 tetrahedra grafts from the Nd(1), as shown in Fig. 2. Viewed along the *a*-axis, the inorganic framework exhibits a zigzag layer structure, between which the ethylenediamine cations and free water molecules are located, as shown in Fig. 3.

The ethylenediamine cations and free water molecules interact with the inorganic framework through N–H⋯O and O–H⋯O hydrogen bonds. There are also hydrogen-bond interactions between the amine molecule and the free water molecule [N(2)⋯O(1W) = 2.906(12) Å] and [N(3)⋯O(2W)#5 = 2.763(11) Å]. The part of H-bonding information is presented in Table 4.
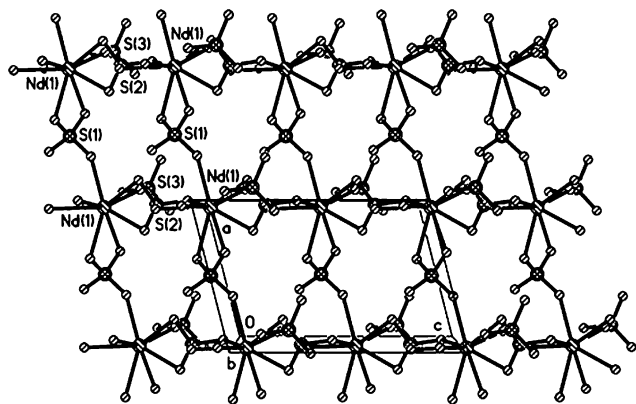
Table 4
Hydrogen bonds (Å and (deg)) for the title compound

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(1)–H(1A)…O(1)#3	0.89	2.36	3.003(10)	129.7
N(1)–H(1A)…O(4)#4	0.89	2.44	2.888(11)	111.7
N(1)–H(1B)…O(7)#4	0.89	2.11	2.956(10)	159.1
N(1)–H(1C)…O(3)#2	0.89	2.08	2.964(10)	171.0
N(2)–H(2A)…O(2)	0.89	2.24	3.053(11)	152.1
N(2)–H(2B)…O(11)#1	0.89	1.96	2.835(11)	166.1
N(2)–H(2C)…O(1W)	0.89	2.06	2.906(12)	158.1
N(2)–H(2C)…O(13)	0.89	2.41	2.873(11)	112.6
N(3)–H(3A)…O(2W)#5	0.89	1.94	2.763(11)	152.2
N(3)–H(3B)…O(10)#6	0.89	2.33	2.962(12)	127.6
N(3)–H(3B)…O(9)#6	0.89	2.54	3.045(11)	116.9
N(3)–H(3C)…O(12)	0.89	1.96	2.833(11)	166.4

Symmetry transformations used to generate equivalent atoms: #1 $x-1,y,z$ #2 $x,-y+3/2,z+1/2$ #3 $x,y,z+1$ #4 $x-1,-y+3/2,z+1/2$ #5 $-x+2,-y+1,-z+1$ #6 $-x+1,-y+1,-z$.

3.3. Fluorescent spectrum

The fluorescent spectrum of the compound was measured in solid state at room temperature. On excitation at 450 nm, this compound gives an emission band at $\lambda_{max} = 622$ nm (Fig. 4). The compound may find potential applications in red-light emitting devices, since it is thermally stable and insoluble in common polar and non-polar solvents.

3.4. Magnetic properties

The temperature dependence magnetic susceptibilities were measured in the temperature range 2–300 K for the compound. Fig. 5 shows the magnetic behavior in the form of the χ_m vs. T and $\chi_m T$ vs. T plots. The measured data are fitted using the Curie–Weiss equation: $\chi_m = C_m/(T - \theta)$, where χ_m is the measured magnetic susceptibility, T the temperature (K), C_m the Curie constant and θ the Weiss constant, with values of the Curie–Weiss constants C_m and θ of 1.53 cm^3 k mol^{-1} and -31.77 K for the title compound, respectively. At 300 K, the calculated effective magnetic moment is $3.31\mu_B$, in good agreement with the expected spin-only value of $3.46\mu_B$ for a f^3 Nd^{3+}. The results indicate the existence of antiferromagnetic interactions.

4. Conclusion

The first organically templated neodymium sulfate with a layer structure has been successfully hydrothermally synthesized in the presence of ethylenediamine as the structure-directing agent. The compound exhibits of a novel two-dimensional zigzag layer structure with 8-membered rings window. The title compound described

Fig. 2. The {Nd(SO_4)_3(H_2O)}_n^{3n-} layer of the compound with the 8-membered ring window, viewed along the *b*-axis.
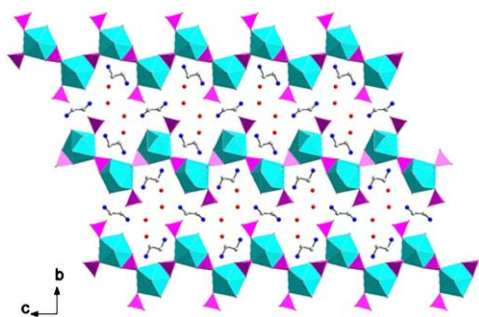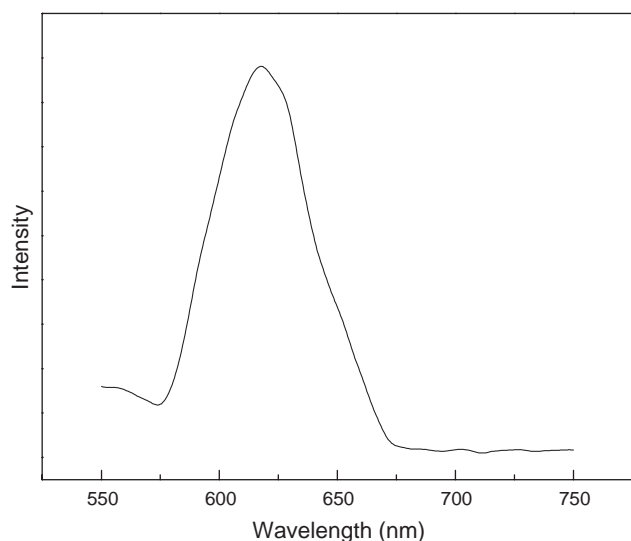

Fig. 3. Polyhedral view of [C_2N_2H_{10}]_{1.5}[Nd(SO_4)_3(H_2O)]·2H_2O with the zigzag layer structure along the *a*-axis, between which the protonated ethylenediamine cations and water molecules are located.

Fig. 4. The solid-state fluorescent spectrum of the compound ($\lambda_{ex} = 450$ nm) at room temperature.
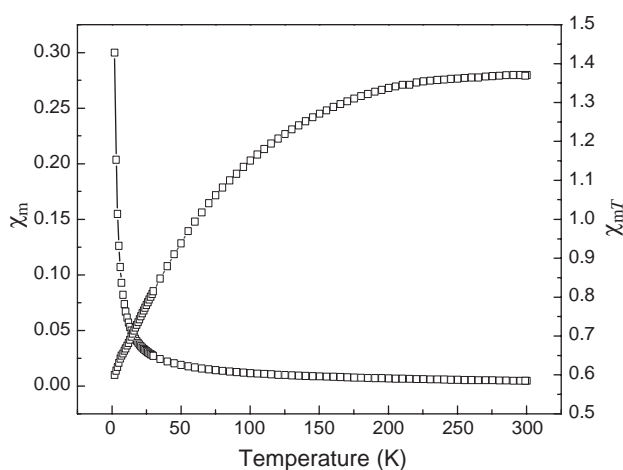

Fig. 5. Plots of χ_m and $\chi_m T$ vs. T for the compound.

in this study demonstrates the possibility of synthesizing new sulfate-based inorganic materials by using structure-directing amines. We are continuing the effort syntheses of new neodymium sulfates by variation of the template agents and crystallization conditions.

5. Supplementary material

Crystallographic data for the structure of the compound reported in this paper have been deposited in the Cambridge Crystallographic Data center as supplementary publication number CCDC 249372. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; *E-mail address*: deposit@ccdc.com. ac.uk).

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