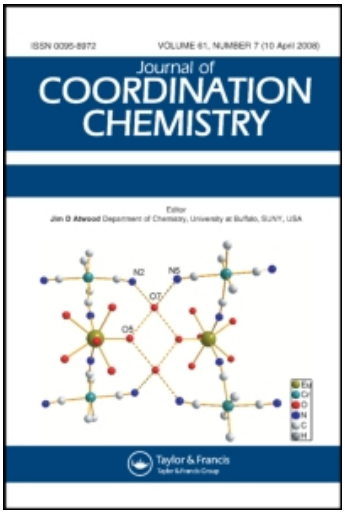

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Syntheses, structures and characterization of the tetranuclear tin(IV) oxysulfide clusters (n-$Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2X_2]$ (X=Cl, Br) (edt=1,2-ethanedithiolate)

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Syntheses, structures and characterization of the tetranuclear tin(IV) oxysulfide clusters $(n\text{-}Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2X_2]$ (X = Cl, Br) (edt = 1,2-ethanedithiolate)

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During attempts to prepare cubane-like clusters from the precursor $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (edt = 1,2-ethanedithiolate), two new tetranuclear tin(IV) oxysulfide clusters, $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Cl_2]$ (**1**) and $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Br_2]$ (**2**) were unexpectedly obtained by reaction of $(Bu_4N)_2[Sn_3S_4(edt)_3]$ with SnX_2 (X = Cl, Br). X-ray crystal structure analyses show that the two compounds possess an isostructural anionic cluster with a highly distorted tetrahedral metal skeleton. The two compounds have been characterized spectroscopically.

Keywords: Cluster; Crystal structure; Tin; Sulfur; Oxysulfide; Spectroscopy

1. Introduction

As analogues of oxide-based zeolites (aluminosilicates and metal phosphates) and other novel functional materials, porous materials and supertetrahedral framework compounds with main group metal chalcogenides have drawn chemists' attention over the last few decades [1–9]. Tin sulfides exhibit abundant structure types because of the versatile coordination characteristics of tin and sulfur. It has been reported that tin sulfide materials have potential applications as micro-porous and semiconductor materials and in solar control devices [10–41]. Many tin(IV) clusters have been synthesized and characterized (e.g., binuclear $Sn_2S_2(S_2CNEt_2)_4$, $Sn_2S_2(SSi(t\text{-}BuO)_3)_4$, $Sn_2S_6^{4-}$ [22–26], trinuclear $[Sn_3S_4(edt)_3]^{2-}$, $[Sn_3S_6Me_6]$, $[Sn_3S_6Ph_6]$ [27–30], tetranuclear $[Sn_4S_6(C_6F_5)_4]$, $[Sn_4S_6(C_6F_5)_4]$, $[Sn_4S_8OCl_4]$ [31–35], pentanuclear $[Sn_5S_{12}]^{4-}$, $(i\text{-}Pr_2Sn)_2(\mu_2\text{-}S)_2(SnS_4)$ [36, 37] and highnuclear clusters $[\{n\text{-}BuSnS(O_2PPh_2)\}_3O]_2Sn$, $[Sn_8S_{12}O_2(OH)_2Cl_6]^{4-}$, $[Sn_{10}O_4S_{16}Cl_4]^{4-}$,

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$[Sn_8S_{12}O_4(SPh)_6]^{6-}$, $[Sn_{10}S_{20}O_4]^{8-}$) [38–40]. In most cases, the complexes were synthesized using one-pot reactions.

Another strategy to design heterometal chalcogenide clusters is to exploit small clusters as precursors or to generate small clusters *in situ* as building blocks to synthesize novel and larger clusters. This approach has been employed successfully to prepare the clusters M/M′/E (M = Cu, Cd, Hg, Zn, Co, Mn, Fe; M′ = Sn, Ge; E = Se, S) [41–51]. To obtain new tin(IV) sulfide oxysulfide clusters, we have explored reactions based on $(Bu_4N)_2[Sn_3S_4(edt)_3]$ and have obtained two new tetranuclear tin(IV) oxysulfide clusters in the presence of SnX_2 (X = Cl, Br). Herein we report the structures and characterization of $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Cl_2]$ (**1**) and $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Br_2]$ (**2**).

2. Experimental

2.1. *Materials and instrumentation*

The starting material $(Bu_4N)_2[Sn_3S_4(edt)_3]$ was prepared according to reference [27]. $SnBr_2$ was synthesized according to the literature [56]. Other chemicals were of reagent grade and used without further purification. Elemental analysis was performed using a Vario EL III system. IR and far-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer (KBr and CsI pellets, respectively). Samples for Raman measurements were diluted by KBr and spectra were recorded on a Nicolet Magna 950 Raman spectrophotometer. ^{1}H NMR spectra (DMSO-d_6) were measured on a Varian Unity-500 spectrometer.

2.2. *$(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Cl_2]$ (1)*

A solution of CH_3CN (6 cm^3) and CH_2Cl_2 (10 cm^3) containing $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (0.125 g, 0.1 mmol) and $SnCl_2 \cdot 2H_2O$ (0.023 g, 0.1 mmol was stirred for 3 h, then filtered, and the filtrate left to stand for one week; colourless blocky crystals of **1** were obtained. The crystals were collected, washed with *i*-propanol and dried in air. Yield: 0.013 g, 9.3% (based on $(Bu_4N)_2[Sn_3S_4(edt)_3]$). Anal. Calcd for $C_{36}H_{80}Cl_2N_2OS_9Sn_4$ (%): C, 31.08; H, 5.80; N, 2.01; Found C, 31.28; H, 5.75; N, 2.12. IR and far-IR (cm^{-1}): 2952(vs), 2927(vs), 2869(vs), 1481(s), 1460(s), 1416(m), 1379(m), 1284(s), 1250(w), 1159(w), 924(s), 876(m), 843(m), 737(w), 669(w), 638(w), 440(m), 431(m), 378(m), 357(m), 343(w), 305(m), 277(m), 199(s); Raman (cm^{-1}): 2991(s), 1117(s), 951(m), 553(s). ^{1}H NMR (ppm): 3.157–3.172(m, 2H, $-CH_2^a$), 2.733–2.872(m, 1H, $-SCH_2$), 1.577(m, 2H, $-CH_b^2$), 1.343–1.301(m, 2H, $-CH_2^c$), 0.954–0.926(m, 3H, $-CH_3^d$), $-NCH_2^dCH_2^cCH_2^bCH_2^a$.

The complex may be prepared by an alternate route. A solution of CH_3CN (5 cm^3) and CH_2Cl_2 (5 cm^3 L) containing $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (0.125 g, 0.1 mmol) and $SnCl_2 \cdot 2H_2O$ (0.023 g, 0.1 mmol) was placed in Parr Teflon lined stainless vessel (25 cm^3), heated at 328 K for 24 h, then cooled slowly to room temperature. The resulting colourless solution was filtered and crystals isolated as above. Yield: 0.080 g, 57.2%.

2.3. $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2Br_2]$ (2)

A solution of CH_3CN (5 cm^3) and CH_2Cl_2 (5 cm^3) containing $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (0.289 g, 0.2 mmol) and $SnBr_2$ (0.057 g, 0.2 mmol) was placed in Parr Teflon lined stainless vessel (25 cm^3). The vessel was heated at 328 for 24 h, then cooled slowly to room temperature. The resulting colourless solution was filtered and crystals of **2** obtained as above. The crystals were washed with diethylether and dried in air. Yield: 0.044 g, 14.9% (based on $(Bu_4N)_2[Sn_3S_4(edt)_3]$). Anal. Calcd for $C_{36}H_{80}Br_2N_2OS_9Sn_4$ (%): C, 29.21; H, 5.45; N, 1.89. Found: C, 29.30; H, 5.40; N, 1.92. IR and far-IR (cm^{-1}): 2954(vs), 2929(vs), 2869(vs), 1477(s), 1465(s), 1416(m), 1377(m); 1290(m), 1250(w), 1147(w), 922(s), 891(m), 870(m), 841(m), 734(w), 667(w), 640(w), 432(s), 378(s), 355(s), 276(m), 224(m), 199(s), Raman (cm^{-1}): 2991(m), 1113(s), 553(m). ^{1}H NMR (ppm): 3.149–3.180(m, 4H, CH_2^a), 2.797–2.874(m, 2H, –SCH_2), 1.570(m, 4H, CH_2^b), 1.335–1.293(m, 2H, CH_2^c), 0.952–0.924(m, 6H, CH_3^d), –$NCH_2^dCH_2^cCH_2^bCH_2^a$.

2.4. *X-ray crystallography*

Crystal data were collected at 293(2) K on a Siemens Smart/CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements were performed with Smart-CCD software. An absorption correction using SADABS software was applied [57]. All non-hydrogen atoms were located by direct methods and refined by full-matrix least-squares techniques. All hydrogen atoms were generated geometrically. Calculations are performed by SHELXL-97 [58]. A summary of crystal data and structure refinement details for the two compounds is provided in table 1. Selected bond lengths and angles for **1** and **2** are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Syntheses*

Reaction of $(Bu_4N)_2[Sn_3S_4(edt)_3]$ with SnX_2 (X = Cl, Br, I) is exemplified in scheme 1. The $Sn(edt)S_2^{2-}$ fragment is present in **1** and **2** and thus the original $[Sn_3S_4(edt)_3]^{2-}$ cluster was destroyed then reassembled to form new tetranuclear tin oxysulfide clusters in the presence of SnX_2 (X = Cl, Br). The oxygen atom lying at the centre of the clusters may come from air, as observed in the formation of some tungsten chalcogenides [52, 53]. It was suggested [32] $SnCl_3^-$ (X = Cl, Br) can be oxidized to Sn(IV) during the preparation of $[P(C_6H_5)_4]_2[Sn_4S_8OCl_4]$ by the reaction of $[P(C_6H_5)_4]SnCl_3$ with Na_2S_4. A similar oxididation took place in the preparation of **1** and **2**.

Compound **1** was easily obtained at room temperature. It was found, however, that the yield of **1** could be improved at higher temperatures. Alternatively, the complex could be prepared by hydrothermal methods reaction. In contrast, compound **2** could not be synthesized at room temperature. The complex was made at 328 K, suggesting that the reactivity of $SnBr_2$ is lower than that of $SnCl_2 \cdot 2H_2O$. Unfortunately, attempts to prepare $(Bu_4N)_2[Sn_4(\mu_4\text{-}O)S_5(edt)_2I_2]$ using SnI_2 were not successful.

Table 1. Crystal data collection and structure refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_{36}H_{80}Cl_2N_2OS_9Sn_4$	$C_{36}H_{80}Br_2N_2OS_9Sn_4$
Formula weight	1391.22	1480.14
Crystal description	Colourless, block	Colourless, block
Dimensions (mm^3)	$0.28 \times 0.26 \times 0.24$	$0.35 \times 0.25 \times 0.24$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unit cell dimensions (Å, °)		
a	16.9229(5)	16.8624(2)
b	17.7833(6)	17.7770(5)
c	19.0944(6)	19.0680(5)
β	90.12(0)	90.031(1)
V ($Å^3$)	5746.4(3)	5715.9(2)
Z	4	4
Index ranges of measured data	−20 to 20, −15 to 21, −22 to 22	−8 to 19, −20 to 16, −21 to 22
θ range for data collection	1.66–25.01	1.66–25.03
μ (mm^{-1})	2.166	3.482
$F(000)$	2784	2928
Reflections measured	11404	8239
Observed reflection	3518 ($>2\sigma(I)$)	3999 ($>2\sigma(I)$)
Independent reflections	5040 ($R_{int} = 0.0466$)	4998 ($R_{int} = 0.0311$)
R	0.0545	0.0722
R_w	0.1201	0.1749
Goodness-of-fit on F^2	1.110	1.185
Largest and mean Δ/σ	0.001, 0.000	0.001, 0.000
Largest difference peaks (e $Å^3$)	0.887, −0.814	0.765, −2.107

$R^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $Rw^b = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; **1**: $a = 0.0258$, $b = 65.2478$; **2**: $a = 0.045$, $b = 173.5088$.

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

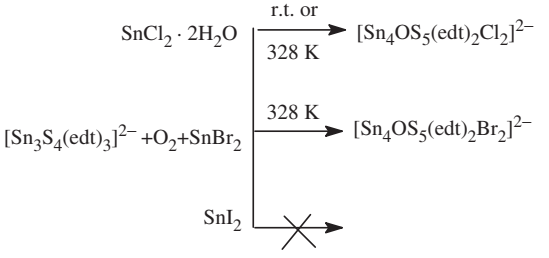
Sn(1)–O(1)	2.268(2)	Sn(1)–S(2)	2.400(2)
Sn(1)–S(5)	2.437(2)	Sn(1)–S(3)	2.449(2)
Sn(1)–S(1)	2.482(2)	Sn(2)–O(1)	2.224(4)
Sn(2)–S(5)	2.390(2)	Sn(2)–S(3)#1	2.397(2)
Sn(2)–S(4)	2.416(2)	Sn(2)–Cl(1)	2.449(2)
O(1)–Sn(1)–S(2)	94.67(17)	O(1)–Sn(1)–S(5)	81.84(9)
S(2)–Sn(1)–S(5)	117.26(9)	O(1)–Sn(1)–S(3)	80.98(9)
S(2)–Sn(1)–S(3)	119.49(9)	S(5)–Sn(1)–S(3)	121.57(8)
O(1)–Sn(1)–S(1)	175.41(17)	S(2)–Sn(1)–S(1)	89.90(9)
S(5)–Sn(1)–S(1)	96.41(9)	S(3)–Sn(1)–S(1)	96.43(9)
O(1)–Sn(2)–S(5)	83.81(8)	O(1)–Sn(2)–S(3)#1	83.05(8)
S(5)–Sn(2)–S(3)#1	128.69(9)	O(1)–Sn(2)–S(4)	86.01(14)
S(5)–Sn(2)–S(4)	115.73(7)	S(3)#1–Sn(2)–S(4)	112.50(6)
O(1)–Sn(2)–Cl(1)	176.84(15)	S(5)–Sn(2)–Cl(1)	94.52(8)
S(3)#1–Sn(2)–Cl(1)	95.97(8)	S(4)–Sn(2)–Cl(1)	97.14(8)
Sn(2)#1–S(3)–Sn(1)	92.24(7)	Sn(2)–S(4)–Sn(2)#1	88.91(10)
Sn(2)–S(5)–Sn(1)	91.42(7)	Sn(2)#1–O(1)–Sn(2)	99.1(3)
Sn(2)#1–O(1)–Sn(1)#1	100.59(7)	Sn(2)–O(1)–Sn(1)#1	102.09(7)
Sn(1)#1–O(1)–Sn(1)	144.7(3)		

Symmetry code #1 is $-x, y, 1/2 - z$.

Table 3. Selected bond lengths (Å) and bond angles (°) for complex **2**.

Sn(1)–O(1)	2.262(3)	Sn(1)–S(2)	2.394(3)
Sn(1)–S(3)	2.429(3)	Sn(1)–S(5)	2.436(3)
Sn(1)–S(1)	2.473(3)	Sn(2)–O(1)	2.227(6)
Sn(2)–S(3)#1	2.388(3)	Sn(2)–S(5)	2.397(3)
Sn(2)–S(4)	2.414(3)	Sn(2)–Br(1)	2.5558(19)
O(1)–Sn(1)–S(2)	94.1(2)	O(1)–Sn(1)–S(3)	81.90(13)
S(2)–Sn(1)–S(3)	116.98(12)	O(1)–Sn(1)–S(5)	81.32(14)
S(2)–Sn(1)–S(5)	119.55(12)	S(3)–Sn(1)–S(5)	121.74(11)
O(1)–Sn(1)–S(1)	175.7(3)	S(2)–Sn(1)–S(1)	90.17(12)
S(3)–Sn(1)–S(1)	96.39(13)	S(5)–Sn(1)–S(1)	96.36(12)
O(1)–Sn(2)–S(3)#1	83.55(12)	O(1)–Sn(2)–S(5)	82.93(11)
S(3)#1–Sn(2)–S(5)	128.64(12)	O(1)–Sn(2)–S(4)	86.5(2)
S(3)#1–Sn(2)–S(4)	115.98(9)	S(4)–Sn(2)–S(4)	112.30(9)
O(1)–Sn(2)–Br(1)	175.83(19)	S(3)#1–Sn(2)–Br(1)	93.64(9)
S(4)–Sn(2)–Br(1)	96.51(9)	S(5)–Sn(2)–Br(1)	97.56(8)
Sn(2)#1–S(3)–Sn(1)	91.48(10)	Sn(2)–S(5)–Sn(1)	92.25(10)
Sn(2)#1–S(4)–Sn(2)	88.62(13)	Sn(2)#1–O(1)–Sn(2)	98.5(4)
Sn(2)#1–O(1)–Sn(1)#1	101.82(11)	Sn(2)–O(1)–Sn(1)#1	100.46(11)
Sn(1)#1–O(1)–Sn(1)	145.6(5)		

Symmetry code #1 is $-x, y, 3/2-z$.



Scheme 1. Assembly of $(Bu_4N)_2[Sn_3S_4(EDT)_3]$ with SnX_2 (X = Cl, Br, I).

3.2. *Structures of 1 and 2*

ORTEP diagrams of the cluster anions of the two compounds are shown in figure 1. The two compounds have a similar cluster structure. The inner cluster core is similar to that observed in $[Sn_4S_8OCl_4]^{2-}$ [32]. In the anion of **1**, the four tin atoms are bridged by O1 to form a highly distorted tetrahedron. Separations of the metal atoms are Sn(1)–Sn(1A) 3.384, Sn(1)–Sn(2) 3.456, Sn(1)–Sn(2A) 3.493 and Sn(2)–Sn(2A) 4.322 Å, respectively, close to those found in $[Sn_4S_8OCl_4]^{2-}$ [32] (3.408, 3.431, 3.438, 4.163 Å). Bond angles M–O–M′ are Sn(2)–O(1)–Sn(2A) 99.1(3), Sn(2)–O(1)–Sn(1A) 102.09(7), Sn(2A)–O(1)–Sn(1A) 100.59(7) and Sn(1A)–O(1)–Sn(1) 144.7(3)°, respectively. Sn1 and Sn(1A) are five-coordinated to two sulfur atoms from one bidentate $SC_2H_4S^{2-}$ ligand, two bridging sulfur atoms and a central oxygen atom (O1), forming a slightly distorted triangular bipyramid. O(1), Sn(1) and S(1) are approximately linear with an angle of 175.41(17)°. Bond angles of O(1)–Sn(1)–S(2) (94.67(17)), O(1)–Sn(1)–S(3) (80.98(9)), O(1)–Sn(1)–S(5) (81.84(9)), S(2)–Sn(1)–S(1) (89.90(9)), S(5)–Sn(1)–S(1) (96.41(9)) and S(3)–Sn(1)–S(1) (96.43(9)°) are all close to 90°. Sn2 and Sn(2A) are bonded to one

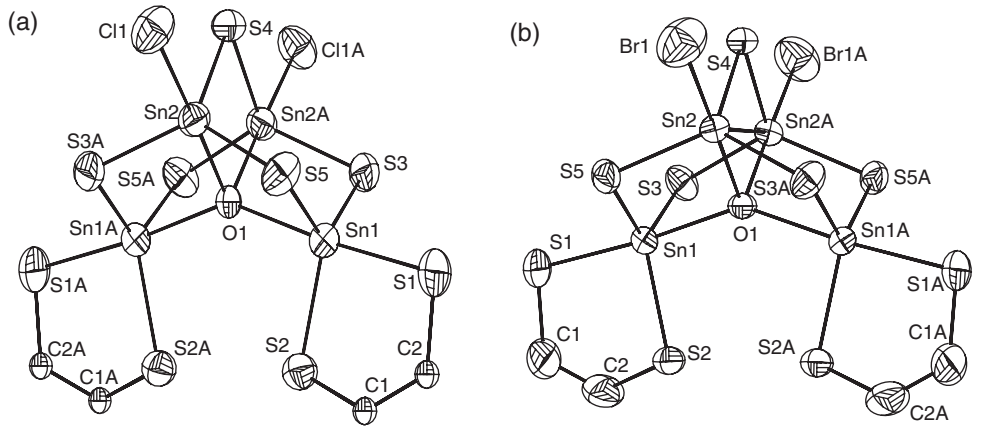


Figure 1. ORTEP diagrams of the anions of complex **1** (a) and complex **2** (b) with the atom numbering scheme (ellipsoids are drawn at 50% probability levels). Symmetry codes (A) for **1** and **2** are $-x$, y, $1/2-z$ and $-x$, y, $3/2-z$, respectively.

terminal chloride, three bridging sulfur and the central O1 atoms, forming a slightly distorted trigonal bipyramid. The Sn–Cl bond length is 2.449(2) Å of Sn–O and Sn–S bond lengths are in the ranges 2.224(4)–2.268(2) and 2.397(2)–2.449(2) Å, respectively.

The structure of the anion of complex **2** is similar to that of **1** except the terminal ligand is Br^-. In the highly distorted tetrahedral metal skeleton, separations of the metal ions, Sn(1)–Sn(1A) (3.373), Sn(1)–Sn(2) (3.484), Sn(1)–Sn(2A) (3.450) and Sn(2)–Sn(2A) (4.322 Å), are slightly shorter than in **1**. The Sn–Br bond length is 2.5558(19) Å and Sn–O and Sn–S bond lengths lie between 2.227(6)–2.262(3) and 2.388(3)–2.429(3) Å, respectively.

3.3. *Spectroscopy*

The ^{1}H NMR spectrum of **1** gives signals corresponding to $-NCH_2^aCH_2^bCH_2^cCH_2^d$ and $-SCH_2CH_2S-$. Compound **2** has a similar spectrum, in agreement with chemical formula and the structural data. IR spectra show peaks for $N(C_4H_9)_4^+$ cations around 2952(vs), 2927(vs), 2869(vs), 1481(s), 1460(s), 1416(m), 1284(s) and 924 cm^{-1}. The weak ν(C–S) peak appears at 640 cm^{-1} [54]. In Raman spectra of **1** and **2**, a strong peak for ν(C–S) was found at 553 cm^{-1}. In far-IR spectra of compounds **1** and **2**, peaks at 440–200 cm^{-1} can be attributed to ν(Sn–S), ν(Sn–O) and ν(Sn–Cl) vibrations [32, 39, 54, 55].

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers for **1** and **2** being 257834 and 257833, respectively. Copies of the data can be obtained free of charge on application

to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail for inquiry: fileserv@ccdc.cam.ac.uk; Email for deposition: deposit@ccdc.cam.ac.uk).

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