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Crystallographic studies on a series of salts of 2,3,7-trihydroxy-9-phenyl-fluorone

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ABSTRACT

2,3,7-Trihydroxy-9-phenyl-fluorone (hereafter H_3Z) has been synthesised in its H_4Z^+ , H_3Z , H_2Z^- and Z^{3-} protonation states. X-ray crystal structure determinations have been carried out for (H_4Z)(HSO₄), H_3Z , [EtⁱPr₂NH]H₂Z, solvated (PPh₄)H₂Z and solvated K₃Z. In each of these salts the 9-phenyl group adopts a different orientation so as to be involved in intermolecular aromatic interactions. The 3- and 6-phenolic carbon–oxygen bond lengths show that double bond character can be delocalised from the ketone to the deprotonated phenoxide across the conjugated π system of the fluorone.

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1. Introduction

2,3,7-Trihydroxy-fluorones, in particular the readily available 9phenyl derivative, **I** (hereafter H₃Z), have been used extensively in the spectrophotometric analysis of a wide range of metals [1]. H₃Z shows amphoteric character as a result of conjugative interactions between the oxygen functions at positions 3- and 6-, as described below. The hydroxy group at position 3- is distinctly more acidic than the remaining two typically phenolic groups at positions 2and 7- as a result of the delocalisation of negative charge in H₂Z⁻ represented by **II** and **III**. Likewise the "quinone-like" C=O group at position 6- is distinctly more basic than normal quinones (or ketones) as a result of the delocalisation of the positive charge following protonation (to give H₄Z⁺) as represented in **IV** and **V**.

We have found only two structural studies in the literature of compounds related to or derived from H₃Z. In 2003 Ward and co-workers [2] reported the structure of a binuclear ruthenium derivative namely {[Ru^{II}(PPh₃)₂(CO)₂]₂Z}⁺PF₆⁻ in which the Z³⁻ ion bridges a pair of Ru^{II} centres. In 2006, the structure of the sulfonated derivative seen in **VI** was reported [3]; interestingly the sulfonic acid residue was present as the sulfonate anion and the fluorone nucleus had been protonated.

Our main interest in these fluorones is in their metal derivatives, but given the paucity of structural data available we considered it worthwhile synthesising and carrying out X-ray structural determinations on crystalline solids containing H_4Z^+ , H_3Z , H_2Z^- and Z^{3-} . Reported below are the syntheses and X-ray crystal structures of $(H_4Z)(HSO_4)$, H_3Z , $[Et^iPr_2NH]H_2Z$, solvated $(PPh_4)H_2Z$ and solvated K_3Z .

2. Experimental

NMR data were collected on a Varian Unity +400 Nuclear Magnetic Resonance Spectrometers. Infrared spectra were recorded using a BioRad 175 FTIR spectrometer. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago, NZ.

2.1. Syntheses

2.1.1. 2,3,7-Trihydroxy-9-phenyl-fluorone (H₃Z)

Benzaldehyde (96 μL, 0.942 mmol) was added to a suspension of 1,2,4-triacetoxybenzene (500 mg, 1.98 mmol) in ethanol (15 mL). Aqueous sulfuric acid (15 vol.%, 15 mL) was then added to the mixture, which was held at 50 °C on a hotplate for four days. H₃Z formed as small orange rod-shaped crystals (104 mg, 0.325 mmol, 35% yield). Infrared, ¹H NMR and ¹³C NMR spectra presented below were carried out on synthesised (not commercially available) fluorone. IR (KBr) 3461, 2451, 1641, 1619, 1532, 1475, 1442, 1416, 1394, 1347, 1297, 1276, 1233, 1205, 1158, 1131, 1030, 958, 865, 844, 828, 797, 772, 740, 707, 699, 656, 627, 603, 599, 577, 449 cm⁻¹. ¹H NMR (400 MHz, *d*₆-DMSO): *δ* 6.79 (s, 2H), 7.28 (s, 2H), 7.51 (m, 2H), 7.72 (m, 3H) ¹³C NMR (100.5 MHz, *d*₆-DMSO): *δ* 102.4, 107.6, 115.8, 128.1, 128.3, 128.9, 129.3, 129.6, 133.3, 147.7.

2.1.2. $H_4Z(HSO_4)$

2,3,7-Trihydroxy-9-phenyl-fluorone (75 mg, 0.234 mmol) was suspended in a mixture of ethanol (2.5 mL) and aqueous sulfuric acid (40 vol.%, 2.5 mL) and held at 50 °C in an oven. Large dark orange hexagonal plate-shaped crystals (33 mg, 0.0789 mmol, 34% yield) formed after three days. IR (KBr): 3112, 1636, 1609, 1561, 1500, 1480, 1445, 1417, 1362, 1272, 1237, 1181, 1128,



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1044, 967, 881, 872, 856, 748, 707, 636, 603, 582, 522, 418 cm⁻¹. ¹H NMR (400 MHz, d_6 -DMSO): δ 6.56 (s, 2H), 6.97 (s, 2H), 7.47 (m, 2H), 7.67 (m, 3H). ¹³C NMR (100.5 MHz, d_6 -DMSO): δ 102.4, 108.7, 116.6, 129.0, 129.3, 130.2, 132.8, 147.9, 153.3, 155.5, 162.1 Anal. Calcd for (HSO₄)(C₁₉H₁₃O₅) C: 54.54 H: 3.37 S: 7.66% Found C: 54.45 H: 3.53 S: 7.88%.

2.1.3. (EtⁱPr₂NH)H₂Z

N-Ethyldiisopropylamine (Hünig's base) (2 mL, 11.5 mmol) was added to a solution of 2,3,7-trihydroxy-9-phenyl-fluorone (200 mg, 0.624 mmol) in boiling DMF (20 mL) and the solution allowed to cool. Large red rod-shaped crystals (113 mg, 0.251 mmol, 40% yield) were collected by vacuum filtration. IR (KBr) 3462, 3235, 2986, 2476, 1634, 1593, 1558, 1546, 1506, 1444, 1348, 1312, 1265, 1235, 1203, 1173, 1128, 1059, 1027, 959, 859, 828, 798, 772, 745, 735, 701, 686, 657, 597, 578, 449, 408 cm⁻¹. ¹H NMR (400 MHz, *d*₆-DMSO): δ 1.07 (m, 12H), 2.78 (m, 2H), 3.13 (m, 3H), 3.29 (m 2H), 6.21 (s, 2H), 6.47 (s, 2H), 7.36 (m, 2H), 7.62 (m, 3H). ¹³C NMR (100.5 MHz, *d*₆-DMSO): δ 14.6, 19.0, 48.60, 48.62, 50.7, 100.9, 104.5, 111.8, 128.6, 128.8, 129.1, 134.4, 146.5, 148.2, 153.1, 167.6. Anal. Calcd for (C₈H₂₀N)(C₁₉H₁₁O₅)-0.1DMF C: 71.77, H: 6.99, N: 3.37%. Found: C: 71.51, H: 6.99, N: 3.49%.

2.1.4. $(Ph_4P)H_2Z \cdot MeOH$

2,3,7-Trihydroxy-9-phenyl-fluorone (100 mg, 0.312 mmol) and tetraphenylphosphonium bromide (393 mg, 0.937 mmol) were suspended in a solution of *N*-ethyldiisopropylamine (160 μ L, 0.937 mmol) in methanol (12 mL) and allowed to stand at room temperature. After 7 days, large red block-shaped crystals (100 mg, 0.145 mmol, 47% yield) formed on the wall of the reaction container. IR (KBr) 3212, 3056, 1639, 1605, 1556, 1543, 1514, 1494, 1438, 1378, 1355, 1265, 1229, 1192, 1160, 1109, 1037, 996, 954, 922, 863, 836, 827, 799, 773, 753, 720, 704, 689, 658, 616, 591, 574, 534, 526, 452, 403 cm⁻¹. ¹H NMR (400 MHz, *d*₆-DMSO): δ 5.10 (s, 2H), 5.28 (s, 2H), 6.38 (s, 2H), 6.61 (s, 3H), 6.83 (m, 20H).

¹³C NMR (100.5 MHz, d_6 -DMSO): δ 99.7, 102.4, 108.6, 117.3, 118.2, 128.5, 129.1, 130.5, 130.6, 134.6, 134.7, 135.5, 148.9, 154.3, 171.1 Anal. Calcd for ($C_{19}H_{11}O_5$)($C_{24}H_{20}P$)·(CH₄O) C: 76.51 H: 5.11% Found C: 76.51 H: 5.33%.

2.1.5. K₃Z·2H₂O·DMSO

A solution of potassium hydroxide (369 mg, 6.59 mmol) in water was added to a suspension of H₃Z (205 mg, 0.640 mmol) in hot dimethylsulfoxide (5 mL). The red plate-shaped crystals (154 mg, 0.281 mmol, 44% yield) that formed were filtered directly from the hot purple solution and washed first with warm dimethylsulfoxide, then chloroform. IR (KBr) 3437, 2926, 2360, 2342, 1626, 1489, 1404, 1385, 1309, 1210, 1176, 1125, 1019, 1008, 832, 770, 703, 668, 658, 579, 451 cm⁻¹. ¹H NMR (400 MHz, D₂O): δ 2.91 (s, 3H, DMSO), 6.07 (s, 2H), 6.44 (s, 2H), 7.18 (m, 3H), 7.40 (s, 2H) ¹³C NMR (100.5 MHz, *d*₆-DMSO): δ 103.25, 106.48, 114.57, 129.53, 129.68, 130.52, 136.28, 154.12, 174.48.

2.2. X-ray crystallography

In each of the structures outlined below, the crystal data are of sufficient quality to enable the phenolic hydrogen atoms to be clearly located. All hydrogen atoms were included at their geometrically estimated positions. Structures 1–5 were solved using direct methods and refined using SHELX-97 [4]. Analytical absorption corrections were applied in the case of structures 1 and 2 using Crysalis CCD software [5].

2.2.1. Crystal data for H_3Z

Crystals of composition $C_{19}H_{12}O_5$ were isolated as orange rods. Crystal dimensions $0.20 \times 0.016 \times 0.015$, Mr = 320.29 g mol⁻¹, monoclinic, space group C2. Collection temperature 130 K, a = 18.3932(6) b = 5.1209(2) c = 15.5362(5) Å, $\beta = 100.376(3)^\circ$, V = 1439.42(9) Å³, Z = 4, $\rho_{calc} = 1.478$ g cm⁻³, $\lambda = 1.54184$ Å $2\theta_{max} = 144.64^\circ$. All non-hydrogen atoms were refined anisotropically. Final *R*1 = 0.0524 ($I > 2\sigma(I)$) for 2046 unique reflections, 257 parameters, *wR*2 = 0.1360, GOF 0.914.

2.2.2. Crystal data for $(H_4Z)(HSO_4)$

C₁₉H₁₄O₉S formed as large brown hexagonal crystals. Crystal dimensions $0.21 \times 0.20 \times 0.10$ mm. $M_r = 418.36$ g mol⁻¹, monoclinic, space group $P2_1/n$. Collection temperature 130 K, a = 12.1173(1) b = 8.9613(10) c = 15.5100(1) Å, $\beta = 94.728(1)^\circ$, V = 1678.45(3) Å³, Z = 4, $\rho_{calc} = 1.656$ g cm⁻³, $\lambda = 1.54184$ Å, $2\theta_{max} = 146.92^\circ$. All non-hydrogen atoms were refined anisotropically. Final R1 = 0.0352 ($I > 2\sigma(I)$) for 3140 unique reflections, 270 parameters, wR2 = 0.1142, GOF 0.909.

2.2.3. Crystal data for (EtⁱPr₂NH)ZH₂

Crystals of C₂₇H₃₁NO₅ formed as red hexagonal plates. Crystal dimensions $0.24 \times 0.18 \times 0.06$ mm, $M_r = 449.53$ g mol⁻¹, monoclinic, space group $P2_1/c$. Collection temperature 130 K, a = 7.7139(8) b = 23.491(3) c = 12.9472(14)Å, $\beta = 93.617(2)^\circ$, V = 2341.5(4)Å³, Z = 4, $\rho_{calc} = 1.275$ g cm⁻³, $\lambda = 0.71073$ Å $2\theta_{max} = 53.48^\circ$. All non-hydrogen atoms were refined anisotropically. Final R1 = 0.0551 ($I > 2\sigma(I)$) for 5297 unique reflections, 319 parameters, wR2 = 0.1287, GOF 0.959.

2.2.4. Crystal data for (PPh₄)(H₂Z)·MeOH

Crystals of $(PC_{24}H_{20})(C_{19}H_{11}O_5)(CH_4O)$ formed as red blocks. Crystal dimensions $0.37 \times 0.30 \times 0.10$ mm, $M_r = 687.67$ g mol⁻¹, triclinic, space group *P*-1. Collection temperature 130 K, a = 9.8493(9) b = 9.9679(9) c = 18.8715(18) Å, $\alpha = 74.888(2)$ $\beta = 75.334(2)$ $\gamma = 86.848(2)^\circ$, V = 1730.3(3) Å³, Z = 2, $\rho_{calc} = 1.320$ g cm⁻³ $\lambda = 0.71073$ Å $2\theta_{max} = 54.74^\circ$. All non-hydrogen atoms were



refined anisotropically. Final $R1 = 0.0530 (I > 2\sigma(I))$ for 7570 unique reflections, 463 parameters, wR2 = 0.1316, GOF 0.952.

2.2.5. Crystal data K₃Z·2H₂O·DMSO

Crystals of K₃C₁₉H₉O₅·2H₂O·C₂H₆SO formed as red plates. Crystal dimensions $0.20 \times 0.07 \times 0.01$ mm, $M_r = 548.72$ g mol⁻¹, triclinic, space group *P*-1. Collection temperature 130 K, *a* = 9.636(3) *b* = 10.002(3) *c* = 12.571(4) Å, $\alpha = 102.087(6) \beta = 90.381(7) \gamma = 98$. 204(6)°, *V* = 1171.8(6) Å³, *Z* = 2 $\rho_{calc} = 1.638$ g cm⁻³, $\lambda = 0.71073$ Å $2\theta_{max} = 53.56^{\circ}$. All non-hydrogen atoms were refined anisotropically. The weakly diffracting nature of these very small crystals resulted in elevated agreement values. Final *R*1 = 0.0951 (*I* > 2 σ (*I*)) for 4047 unique reflections, 298 parameters, *w*R2 = 0.1992, GOF 0.931.

3. Results and discussion

$3.1. H_3Z$

The neutral form of the fluorone, H_3Z , was prepared by heating a suspension of 1,2,4-triacetoxybenzene in a solution of benzaldehyde, ethanol and aqueous sulfuric acid. The fluorone unit itself is very close to being planar, with the 9-phenyl ring disordered over two orientations of equal occupancy. The two orientations are inclined to the plane of the fluorone by 64.9(3) and 117.2(2)°. The 3-phenolic carbon–oxygen bond (1.335(5) Å), although longer than the carbonyl C=O double bond (1.281(5) Å), is shorter than the other phenolic carbon–oxygen bonds (1.362(5) Å). This is indicative of partial double bond character with some delocalisation from the 6-carbonyl group across the aromatic fluorone unit and into the 3-carbon–oxygen bond, as described in the introduction. A list of phenyl group – fluorone angles and selected carbon– oxygen bond lengths is presented in Table 1 (Fig. 1).

Hydrogen bonds between fluorone units result in the formation of chains, shown in Fig. 2. The chains align themselves into layers with all chains in a given layer running parallel to each other.

Layers stack in an ABAB fashion in the *c*-direction, with all chains within a single layer running parallel to each other. The direction of the chains in the 'A' layers differs by approximately 80° to the direction of the chains in the 'B' layers. The chains in one layer hydrogen bond to the chains in one neighbouring layer to form a bilayer. Two different views of the bilayers are presented in Fig. 3a and b. The 9-phenyl groups extend above and below this bilayer. Fig. 3b shows

Table 1				
Selected bond lengths and	d angles	of the	fluorone	species.



Fig. 1. The H_3Z asymmetric unit. Thermal ellipsoids are at the 50% probability level. The phenyl ring is disordered over two orientations, each with 50% occupancy, only one of which is shown here.



Fig. 2. One layer of H_{3Z} hydrogen bonded chains, as viewed from above. The phenyl ring on any given fluorone has the opposite orientation to those on the fluorone units immediately beside it. Within a single chain the phenyl groups do not necessarily have the same orientation.

a single bilayer represented by dark bonds. The phenyl groups oriented up and down interdigitate with those of adjacent bilayers.

3.2. (H₄Z)(HSO₄)

 $(H_4Z)(HSO_4)$ was prepared by heating H_3Z in an aqueous ethanol/sulfuric acid mixture. The protonation of the fluorone unit leads to the lengthening of the carbon–oxygen bond in the 6-position to 1.335(2) Å. The three phenolic carbon–oxygen bonds have lengths of 1.367(2), 1.354(2) and 1.339(2) Å (Fig. 4).

The fluorone cation and bisulfate anions interact via hydrogen bonds. Each ion is involved in five hydrogen bonds. The fluorone cation acts as the hydrogen bond donor in four of these interactions and as the acceptor in the remaining one. Conversely, the bisulfate anion acts as the donor in only one of its hydrogen bonds and the acceptor in the remaining four. This series of hydrogen bonds results in the formation of a complex three-dimensional hydrogen bonded network.

	C6–O6 (Å)	C3–O3 (Å)	C2–O2 (Å)	C7–O7 (Å)	Angle between phenyl ring and fluorone (°)
H₃Z	1.281(5)	1.335(5)	1.362(5)	1.362(5)	117.2(2) and 64.9(3)
$(H_4Z)(HSO_4)$	1.335(2)	1.339(2)	1.367(2)	1.354(2)	63.0(5)
(HNEt ⁱ Pr ₂)(H ₂ Z)	1.265(2)	1.291(2)	1.359(2)	1.357(2)	73.9(6)
$(PPh_4)(H_2Z)$	1.272(2)	1.288(2)	1.359(2)	1.359(2)	67.7(6)
K ₃ Z	1.28(1)	1.29(1)	1.33(1)	1.30(1)	72.4(3)





Fig. 3. (a) The H_3Z hydrogen bonded bilayer. Chains within a single layer are shown in the same shade. Hydrogen bonds are represented by black and white striped bonds. (b) The phenyl groups of two adjacent bilayers interdigitate. Both orientations of the phenyl rings are shown. Hydrogen bonds between fluorone units are not shown.

3.3. [EtⁱPr₂NH]H₂Z

 $(HNEt^iPr_2)H_2Z$, Fig. 5, was obtained by cooling a hot DMF solution of Hünig's base and H_3Z . As expected, the phenol group in the 3-position is deprotonated. The carbon–oxygen bonds in the 6- and 3-positions are 1.265(2) and 1.291(2) Å respectively, which is consistent with significant double bond character in both bonds. The 2- and 7-phenolic carbon–oxygen single bonds have lengths of 1.359(2) and 1.357(2) Å. The terminal carbon on the ethyl group on the trialkylammonium cation is disordered over several sites.

In the solid state, each H_2Z^- unit forms hydrogen bonds to an ethyldiisopropylammonium cation and to three other fluorones. This results in a two-dimensional net of (6,3) topology, shown in Fig. 6. The sheets are arranged such that the spaces in each sheet are located directly above the spaces in the sheet below leading to the formation of channels. The trialkylammonium cations are located within these channels.

3.4. (PPh₄)H₂Z·MeOH

Crystals of (PPh₄) H_2Z ·MeOH were obtained from a mixture of H_3Z , PPh₄Br and Hünig's base in methanol upon standing. These



Fig. 4. A representation of the hydrogen bonds in $(H_4Z)(HSO_4)$ surrounding (a) the fluorone cation and (b) the bisulfate anion. Each fluorone cation forms hydrogen bonds to five bisulfate anions and each bisulfate anion hydrogen bonds to five fluorone cations. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms bound to carbon atoms have been removed from (b) for clarity.

crystals have edge lengths of several millimeters. The crystals have a deep green, lustrous, highly reflective appearance when viewed with reflected light however, the crystals appear red and transparent under transmitted light.



Fig. 5. The asymmetric unit of $(HNEt^iPr_2)H_2Z$. Only one orientation of the trialkylammonium cation is shown, and aliphatic hydrogen atoms have been omitted for clarity. The thermal ellipsoids are at 50% probability level.



Fig. 6. The $(HNEt^{i}Pr_{2})H_{2}Z$ hydrogen bonded sheets. The trialkylammonium cations sit in the spaces within the sheets and are shown in black. Only one orientation of the trialkylammonium cations is shown.



Fig. 7. The cations in $(PPh_4)H_2Z$.MeOH surrounded by hydrogen bonded fluorone chains. The phenyl ring on the H_2Z anion is involved in an edge-to-face interaction with one ring on the PPh_4 cation. Methanol molecules are not shown.



Fig. 8. A 2D sheet resulting from potassium–fluorone interactions within K_3Z -DMSO-2H₂O. The potassium–oxygen interactions are shown as darker. Potassium atoms are shown as large dark spheres and DMSO atoms are represented as open circles.



Fig. 9. The three-dimensional network of K₃Z·DMSO·2H₂O. The sheets depicted in Fig 8 extend horizontally into the plane of the page and are bridged by solvent water molecules. Solvent water molecules are shown as hatched circles and the atoms of DMSO are shown as open circles.

The carbon–oxygen bond involving the 3-phenoxy group in this instance, as in the trialkylammonium salt, shows a very marked shortening compared to that in the H_3Z species, similar to that found in the (Et^iPr_2NH) H_2Z salt described above. In (PPh₄) H_2Z , the 3- and 6-carbon–oxygen bonds have lengths of 1.288(2) and 1.272(2) Å, respectively. The carbon–oxygen framework of the fluorone monoanion is essentially identical to that observed in the trialkylammonium salt discussed above. For corresponding bonds in the PPh₄ and HNⁱPr₂Et salts, the largest variation in bond length between these two structures is approximately 0.02 Å.

As in the H_3Z structure, the fluorone units form hydrogen bonds leading to the formation of chains (Fig. 7). These chains all run parallel, trapping the PPh₄ cations in the spaces between them. The 9phenyl ring is inclined to the plane of the fluorone by a dihedral angle of 67.7(6)°, which allows it to participate in edge-to-face aromatic interactions with one of the phenyl rings of a PPh₄ cation.

3.5. K₃Z·2H₂O·DMSO

The addition of aqueous KOH to a suspension of H_3Z in hot DMSO led to the formation of hygroscopic red crystals with green iridescence. Each Z^{3-} unit is associated with nine potassium centres. In addition to the expected short carbon–oxygen bonds at positions 3- and 6- on the fluorone (1.29(1) and 1.28(1) Å, respectively) the two remaining hydroxyl C–O distances are shorter than those observed in the two H_2Z^- salts: 1.33(1) and 1.30(1) Å in Z^{3-} , 1.354(2)–1.367(2) Å in the H_2Z^- structures. There are three crystallographically distinct K⁺ ions each of which links to three Z^{3-} units. Each Z^{3-} unit in turn interacts with nine potassium ions with K–O distances ranging from 2.63(1) to 3.03(1) Å.

As indicated in Fig. 8, a two-dimensional network is formed through interaction of Z^{3-} with K^+ ions. The network is further supported by bridging oxygen atoms belonging to DMSO molecules.

The phenyl ring of the fluorone is inclined to the fluorone by 72.4(3)°. This phenyl ring participates in a pair of edge to face interactions with a catechol-like group from the same sheet and another catechol-like group belonging to an adjacent sheet. Water molecules bridge potassium ions from adjacent sheets leading to the generation of a three-dimensional network, Fig. 9.

4. Concluding remarks

The 9-phenyl-2,3,7-trihydroxyfluor-6-one has been synthesised and structurally characterised in four different protonation states – H_4Z^+ , H_3Z , H_2Z^- and Z^{3-} . The 3- and 6-phenolic carbon-oxygen bond lengths indicate that double bond character is delocalised across the conjugated π system from the ketone to the deprotonated phenoxide. The orientation of the 9-phenyl ring with respect to the fluorone unit varies from compound to compound in order to participate in intermolecular aromatic interactions.

5. Supporting Information

CCDC 705417–705421 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033).

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