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Synthesis and Structure of Bis(monohaloacetates) of Tris(5-bromo-2-methoxyphenyl)antimony

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Abstract—Tris(5-bromo-2-methoxyphenyl)antimony bis(monohaloacetates) $[(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb[OC(O)CH_2X]_2$, X = Cl (**I**), Br (**II**), I (**III**) have been synthesized by the reaction of tris(5-bromo-2-methoxyphenyl)antimony with chloro-, bromo-, and iodoacetic acids in the presence of hydrogen peroxide. According to X-ray analysis the antimony atom in **I–III** has a distorted trigonal-bipyramidal coordination.

Keywords: tris(5-bromo-2-methoxyphenyl)antimony, haloacetic acids, oxidative addition, hydrogen peroxide, molecular structure

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The majority of the synthesized and structurally characterized triaryantimony dicarboxylates contain the phenyl group [1]. As to other aryl residues, antimony dicarboxylates may contain *p*- and *m*-tolyl [2–7], *p*-chloro [8], *p*-fluoro [9], *p*-trifluoromethyl [2], *p*-*N*,*N*-dimethylaminophenyl [10–12] groups. The effect of substituents in aromatic rings on the structure of triarylantimony dicarboxylates or the character of coordination of the carboxylic ligands was not established. The synthesis and structural studies of tris(5-bromo-2-methoxyphenyl)antimony dicarboxylates are described in [13–15]. A specific structural feature of $[(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb[OC(O)R]_2$ (R = $C_6H_4NO_2$-2, *cyclo*-C_3H_6, $CH_2C_6H_4NO_2$-4, $C_6H_4OCH_3$-2, $C{\equiv}CC_6H_5$) is the presence of two types of intramolecular contacts (Sb···O=C and Sb···OMe), which allows to regard these derivatives as complexes of highly coordinated antimony.

It was of interest to establish the factors affecting the strength of binding of the carboxylate ligands and the asymmetry of their coordination to the antimony atom in this type of compounds.

Since the intramolecular contact Sb···O=C arises from the donor-acceptor interaction, its strength largely depends on donor properties of the carbonyl oxygen, which, in turn, are determined by the nature of organic residue. Thus, residue R with *–I*-effect lowers the donating ability of the carbonyl oxygen, which must decrease the strength of its binding with the antimony atom.

The influence of the inductive effect of organic residue on the electron density distribution in the carboxylic group can be followed by the example of monohaloacetic acids, in which the *–I*-effect is decreased from chlorine to iodine.

Tris(5-bromo-2-methoxyphenyl)antimony bis(monohaloacetates) were synthesized by the reaction of oxidative addition of tris(5-bromo-2-methoxyphenyl)antimony with monohaloacetic acids in the presence of hydrogen peroxide [16] in 91–94 % yield.

$$[(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb + 2\ HOC(O)CH_2X + H_2O_2$$
$$\rightarrow [(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb[OC(O)CH_2X]_2 + 2H_2O,$$
$$X = Cl\ (\mathbf{I}),\ Br\ (\mathbf{II}),\ I\ (\mathbf{III}).$$

The structure of the obtained compounds was investigated by IR, ^1H, ^{13}C NMR spectroscopy and X-ray diffraction (XRD) analysis. In the IR spectra of compounds **I–III** the absorption bands of the stretching vibrations of the carbonyl groups (1663, 1662, 1657 cm^{-1} respectively) are shifted to long waves relative to the corresponding bands of free acids (1734, 1726, 1718 cm^{-1}), which is typical of the formation of chelate structures [17].

^1H NMR spectra of complexes **I–III** contain singlet signals of the methylene protons CH_2 and methoxy

Table 1. Crystallographic data, experimental and refining parameters for structures **I–III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{25}H_{22}Br_3Cl_2O_7Sb$	$C_{25}H_{22}Br_5O_7Sb$	$C_{25}H_{22}O_7Br_3I_2Sb$
M	866.79	955.69	1049.69
Cristal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a, Å	9.5617(6)	9.5782(4)	9.6110(4)
b, Å	12.0598(8)	12.2047(6)	12.4357(6)
c, Å	15.1168(9)	15.1414(7)	15.3644(8)
α, deg	108.803(2)	109.543(2)	110.471(2)
β, deg	94.740(2)	94.658(2)	95.182(2)
γ, deg	112.117(2)	111.1280(10)	109.458(2)
V, Å^3	1486.77(17)	1514.37(12)	1577.03(13)
Z	2	2	2
d_{calc}, g/cm^3	1.936	2.096	2.211
μ, mm^{-1}	5.180	7.548	6.672
F(000)	836.0	908.0	980.0
Crystal size, mm	0.42 × 0.28 × 0.13	0.37 × 0.27 × 0.21	0.25 × 0.2 × 0.1
θ range, deg	2.93°–23.87°	3.04°–22.07°	3.01°–25.6°
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 16$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-18 \le l \le 18$
Reflections measured	46423	6224	20139
Independent reflections	4596	3741	5932
R_{int}	0.0266	0.0201	0.0327
Number of refined parameters	346	346	346
GOOF	1.041	1.052	1.022
R-factors on $F^2 > 2\sigma(F^2)$	R_1 0.0265, wR_2 0.0612	R_1 0.0317, wR_2 0.0818	R_1 0.0321, wR_2 0.0720
R-factors (all data)	R_1 0.0311, wR_2 0.0641	R_1 0.0392, wR_2 0.0859	R_1 0.0487, wR_2 0.0791
Residual electron density (min/max), *e*/A^3	0.83/–0.94	0.90/–1.16	0.81/–1.46

groups OCH_3 of bromoanisyl residues with the ratio of integral intensities of 4 : 9. In the range of 6.91–8.07 ppm the signals of three non-equivalent aromatic protons appear (the ratio of integral intensities 3 : 3 : 3) (Table 1).

The ^{13}C NMR spectra contain the signals of the methylene carbons CH_2Hal shifted downfield with respect to those of free acids [17]. The position of the carbonyl carbon signal of **I–III** only slightly depends on the nature of the halogen atom. The signals of the methoxy carbons and of six non-equivalent aromatic carbons in **I–III** are also close to each other.

According to the XRD data the antimony atom in molecules **I, II, III** has a distorted trigonal bipyramidal coordination (Figs. 1–3). Principal crystallographic data and the results of refinement of the structures are

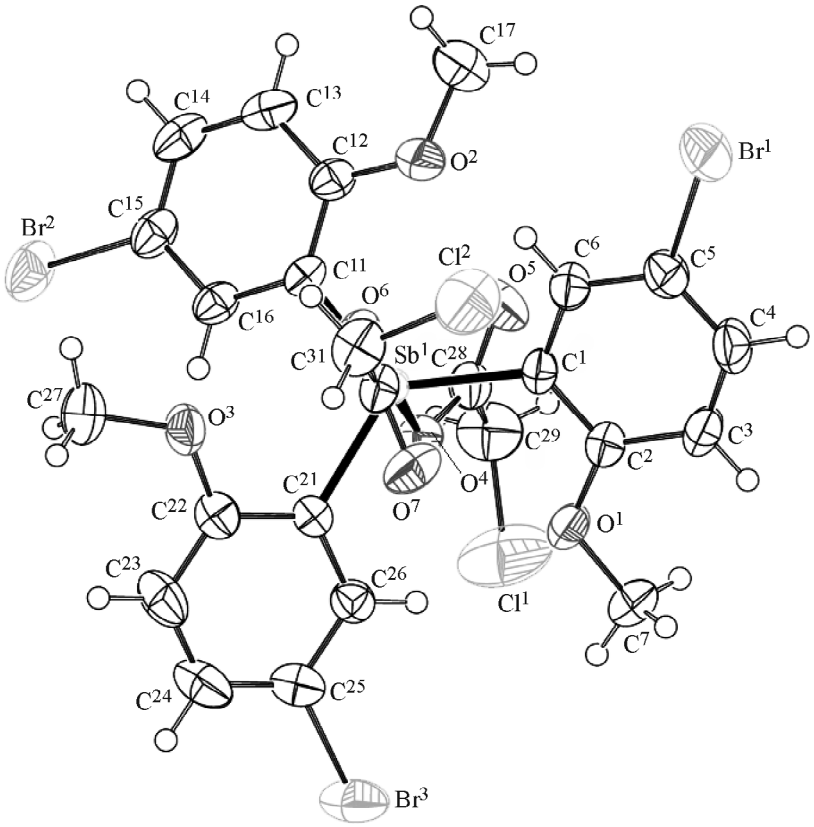

Fig. 1. General view of compound **I**.

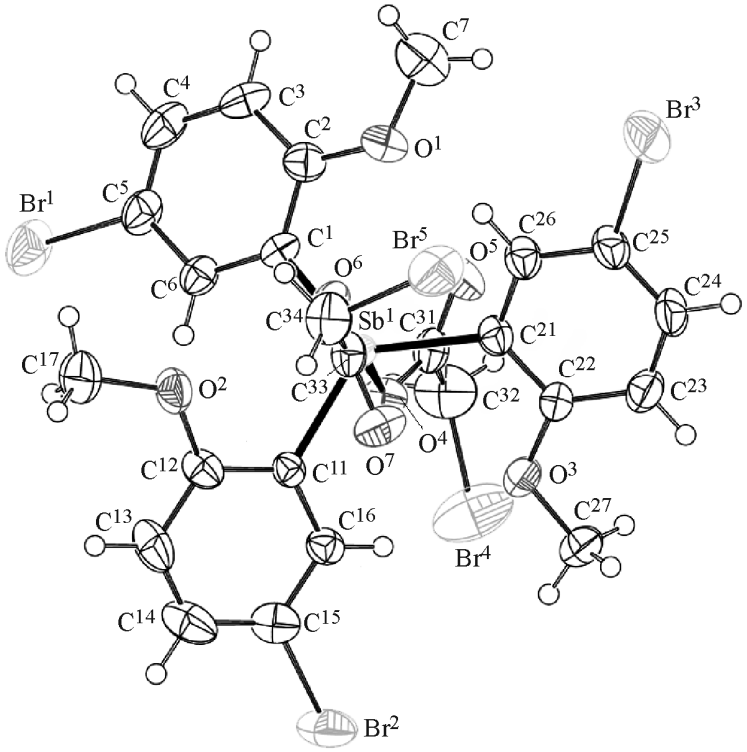

Fig. 2. General view of compound **II**.

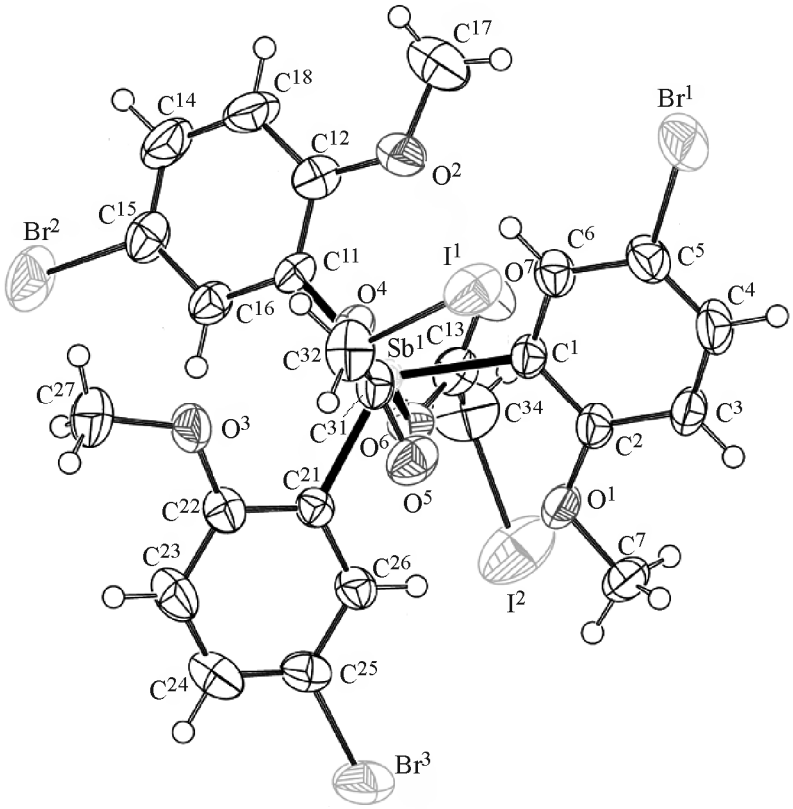

Fig. 3. General view of compound **III**.

presented in Table 1, the main bond distances and bond lengths are given in Table 2. Axial angles OSbO in **I–III** are close to 180°. The antimony atoms are displaced from the equatorial plane C_3 by 0.030, 0.028, 0.025 Å respectively. The sum of angles in the equatorial plane CSbC is close to the ideal value.

Mean values of the Sb–C and Sb–O bond distances have close values (Table 2).

Molecules **I–III** do not possess *cis*-orientation of the carboxylate ligands relative to the SbC_3 fragment common for triphenylantimony dicarboxylates [18]. The angles between the carboxylic group planes are equal to 48.37º (**I**), 48.92º (**II**), 50.44º (**III**), therefore the carbonyl oxygen atoms are located opposite to different equatorial angles, which are increased relative to the ideal one, whereas the third angle is decreased (Table 2). The same orientation of the carboxylate groups and similar values of equatorial angles are observed also in the molecules of other tris(5-bromo-2-methoxyphenyl)antimony dicarboxylates [13–15].

Carboxylate ligands show anisobidentate binding character: see $Sb^1\cdots O^5$ and $Sb^1\cdots O^7$ distances in **I–III** (Table 2). Thus, in **I–III** we observe a strengthening of binding of the carboxylate ligands with the decrease of the negative inductive effect of the residue.

Along with intramolecular interactions Sb···O=C in **I–III**, there are contacts Sb···OMe (3.120(3)–3.173(3) Å, 3.107(5)–3.171(4) Å, 3.104(4)–3.170(4) Å respectively). The analysis of the structures under consideration shows that the Sb···OMe distance is to a large extent determined by geometric factor, namely, the angle of rotation of the aromatic ring with respect to the equatorial plane.

Apparently, the reason for unusual orientation of the carboxylate groups with respect to each other is nonvalent interactions Sb···OMe in molecules **I, II, III**.

Structural organization in the crystal is due to weak hydrogen bonds of the C=O···H–C and C–Br···H–C types. Oxygen atoms of the methoxy groups are not involved in the intermolecular interactions.

Therefore, in compounds **I, II, III** the intramolecular interactions Sb···O=C grow with the decrease in the electronegativity of the halogen atom in monohaloacetic acid. The coordination of the antimony atom

Table 2. Bond distances and bond angles for structures **I–III**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
			I				
$Sb^1–O^4$	2.116(2)	$O^4Sb^1O^6$	177.23(9)	$C^{30}–O^6$	1.300(5)	$C^1Sb^1O^6$	87.42(12)
$Sb^1–O^6$	2.115(2)	$C^1Sb^1C^{11}$	124.59(14)	$C^{30}–O^7$	1.211(5)	$C^{11}Sb^1O^6$	87.64(11)
$Sb^1–C^1$	2.112(3)	$C^1Sb^1C^{21}$	124.83(14)	$Sb^1\cdots O^1$	3.134(2)	$C^{21}Sb^1O^6$	97.85(12)
$Sb^1–C^{11}$	2.105(3)	$C^{11}Sb^1C^{21}$	110.53(14)	$Sb^1\cdots O^2$	3.173(3)	$O^4C^{28}O^5$	125.2(4)
$Sb^1–C^{21}$	2.108(3)	$C^{21}Sb^1O^4$	83.36(12)	$Sb^1\cdots O^3$	3.120(3)	$O^6C^{30}O^7$	124.2(4)
$C^{28}–O^4$	1.288(4)	$C^1Sb^1O^4$	93.95(12)	$Sb^1\cdots O^5$	3.190(4)		
$C^{28}–O^5$	1.210(5)	$C^{11}Sb1O^4$	89.60(12)	$Sb^1\cdots O^7$	3.016(3)		
			II				
$Sb^1–O^4$	2.121(4)	$O^4Sb^1O^6$	177.28(16)	$C^{33}–O^6$	1.304(8)	$C^1Sb^1O^6$	87.76(19)
$Sb^1–O^6$	2.114(4)	$C^1Sb^1C^{11}$	100.6(2)	$C^{33}–O^7$	1.205(8)	$C^{11}Sb^1O^6$	97.70(19)
$Sb^1–C^1$	2.108(6)	$C^1Sb^1C^{21}$	124.5(2)	$Sb^1\cdots O^1$	3.171(4)	$C^{21}Sb^1O^6$	87.29(19)
$Sb^1–C^{11}$	2.117(5)	$C^{11}Sb^1C^{21}$	124.9(2)	$Sb^1\cdots O^2$	3.107(5)	$O^4C^{31}O^5$	126.3(6)
$Sb^1–C^{21}$	2.111(6)	$C^{21}Sb^1O^4$	94.46(19)	$Sb^1\cdots O^3$	3.129(4)	$O^6C^{33}O^7$	123.6(6)
$C^{31}–O^4$	1.282(7)	$C^{11}Sb^1O^4$	83.01(18)	$Sb^1\cdots O^5$	3.192(6)		
$C^{31}–O^5$	1.211(8)	$C^1Sb^1O^4$	89.54(19)	$Sb^1\cdots O^7$	2.994(5)		
			III				
$Sb^1–O^4$	2.116(3)	$O^4Sb^1O^6$	176.72(12)	$C^{33}–O^6$	1.293(6)	$C^1Sb^1O^6$	95.33(16)
$Sb^1–O^6$	2.111(3)	$C^1Sb^1C^{11}$	125.05(18)	$C^{33}–O^7$	1.212(6)	$C^{11}Sb^1O^6$	89.07(15)
$Sb^1–C^1$	2.116(4)	$C^1Sb^1C^{21}$	124.72(17)	$Sb^1\cdots O^1$	3.123(3)	$C^{21}Sb^1O^6$	82.67(15)
$Sb^1–C^{11}$	2.110(4)	$C^{11}Sb^1C^{21}$	110.19(17)	$Sb^1\cdots O^2$	3.170(4)	$O^4C^{31}O^5$	123.7(5)
$Sb^1–C^{21}$	2.116(4)	$C^{21}Sb^1O^4$	97.70(15)	$Sb^1\cdots O^3$	3.104(4)	$O^6C^{33}O^7$	124.6(5)
$C^{31}–O^4$	1.300(6)	$C^1Sb^1O^4$	87.14(15)	$Sb^1\cdots O^5$	2.986(5)		
$C^{31}–O^5$	1.215(6)	$C^{11}Sb1O^4$	87.75(15)	$Sb^1\cdots O^7$	3.174(5)		

to the three oxygen atoms of methoxy groups of aryl residues results in an unusual orientation of the carboxy groups with respect to the SbC_3 fragment.

EXPERIMENTAL

Synthesis of tris(5-bromo-2-methoxyphenyl)antimony bis(monohaloacetates) (general procedure). To the solution of 0.30 g (0.44 mmol) of tris(5-bromo-2-methoxyphenyl)antimony in 30 mL of diethyl ether 0.083 g (0.88 mmol) of monohaloacetic acid and 0.05 mL (0.44 mmol) of 30% aqueous solution of hydrogen peroxide was added. The reaction mixture was kept at 20°C for 24 h. After removal of the solvent the target products were obtained.

$[(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb[OC(O)CH_2Cl]_2$ (I). Yield 0.36 g (94 %), colorless crystals, t.decomp. 206-207°C. IR spectrum, (ν, cm^{-1}): 3101, 3079, 2993,

2937, 2838, 1663, 1574, 1477, 1437, 1415, 1377, 1324, 1282, 1256, 1185, 1166, 1148, 1131, 1096, 1045, 1013, 926, 891, 882, 828, 810, 783, 708, 671, 621, 586, 522, 485, 449. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.03 d (*J* = 2.38, 3H), 7.58 d.d (*J* = 2.36, 8.79, 3H), 6.93 d (*J* = 8.86, 3H), 3.88 s (9H), 3.74 s (4H). ^{13}C NMR spectrum, δ, ppm: 169.42 (C=O), 158.90, 137.15, 135.63, 128.97, 114.08, 113.51 (C–Ar), 56.32 (CH_3O), 42.50 (CH_2). Found, %: C 34.46; H 2.59. $C_{25}H_{22}Br_3Cl_2O_7Sb$. Calculated, %: C 34.60; H 2.54.

[(5-Br)(2-MeO)C_6H_3]$_3$Sb[OC(O)CH_2Br]$_2$ (II). Yield 0.38 g (91%), crystals with t.decomp. 235°C. IR spectrum, (ν, cm^{-1}): 3101, 3074, 2993, 2937, 2839, 1662, 1574, 1476, 1437, 1378, 1314, 1282, 1256, 1218, 1203, 1186, 1148, 1099, 1046, 1014, 930, 892, 826, 809, 683, 621, 563, 449. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.05 d (*J* = 2.36, 3H), 7.58 d.d (*J* = 2.36, 8.78, 3H), 6.93 d (*J* = 8.84, 3H), 3.88 s (9H), 3.54 s (4H). ^{13}C NMR spectrum, δ, ppm: 169.15 (C=O), 158.77, 137.07, 135.40, 128.65, 113.87, 113.26 (C–Ar), 56.18 (CH_3O), 28.54 (CH_2). Found, %: C 31.09; H 2.49. $C_{25}H_{22}Br_5O_7Sb$. Calculated, %: C 31.38; H 2.30.

[(5-Br)(2-MeO)C_6H_3]$_3$Sb[OC(O)CH_2I]$_2$ (III). Yield 0.43 g (93%), crystals with t.decomp. 168-169°C. IR spectrum, (ν, cm^{-1}): 3100, 2992, 2938, 2839, 1657, 1574, 1475, 1437, 1416, 1377, 1308, 1282, 1255, 1184, 1149, 1092, 1078, 1046, 1014, 932, 884, 826, 809, 677, 622, 538, 448. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.07 d (*J* = 2.36, 3H), 7.57 d.d (*J* = 2.36, 8.82, 3H), 6.93 d (*J* = 8.82, 3H), 3.91 s (9H), 3.38 s (4H). ^{13}C NMR spectrum, δ, ppm: 170.79 (C=O), 158.93, 137.33, 135.50, 128.80, 113.99, 113.34 (C–Ar), 56.43 (CH_3O), –1.00 (CH_2). Found, %: C 28.23; H 2.12. $C_{25}H_{22}Br_3I_2O_7Sb$. Calculated, %: C 28.57; H 2.09.

IR spectra of compounds **I–III** were taken on a Bruker Tensor 27 spectrometer in KBr in the range 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were registered on an Agilent DD2 400 NMR spectrometer (working frequency 400 MHz), internal reference HMDS, solvent chloroform.

X-Ray structural analysis on single crystals **I, II, III** was performed on a D8 QUEST Bruker diffractometer (Mo K_a-radiation, λ = 0.71073 Å, graphite monochromator) at 273 K. Collection, processing of the data and refinement of the unit cell parameters, as well as correction for the extinction were performed using the SMART and SAINT-*Plus* programs [19]. All calculations on solution and refinement of the structure were performed using the SHELXL/PC program package [20]. The structures were solved by direct method and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms.

Full tables of atomic coordinates, bond distances, and bond angles are deposited to the Cambridge Crystallographic Data Centre (nos. 993551-993553) deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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