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Novel peroxosolvates of quinolone antibiotics containing large hydrogen peroxide clusters

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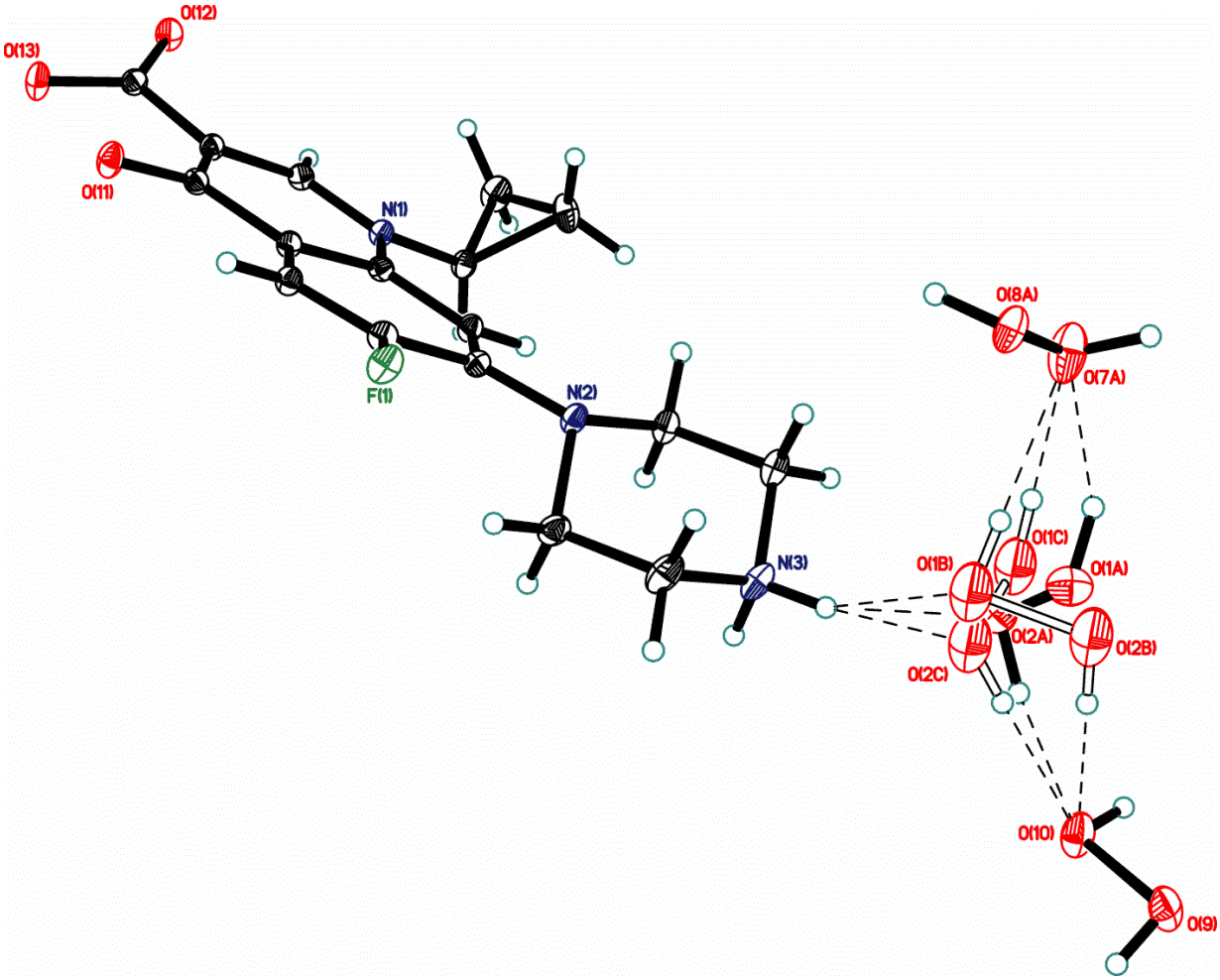

Figure S1 Hydrogen bonds (dashed lines) formed by peroxide molecule H1-O1-O2-H2 in **2**. Minor components of disorder are shown as open lines.

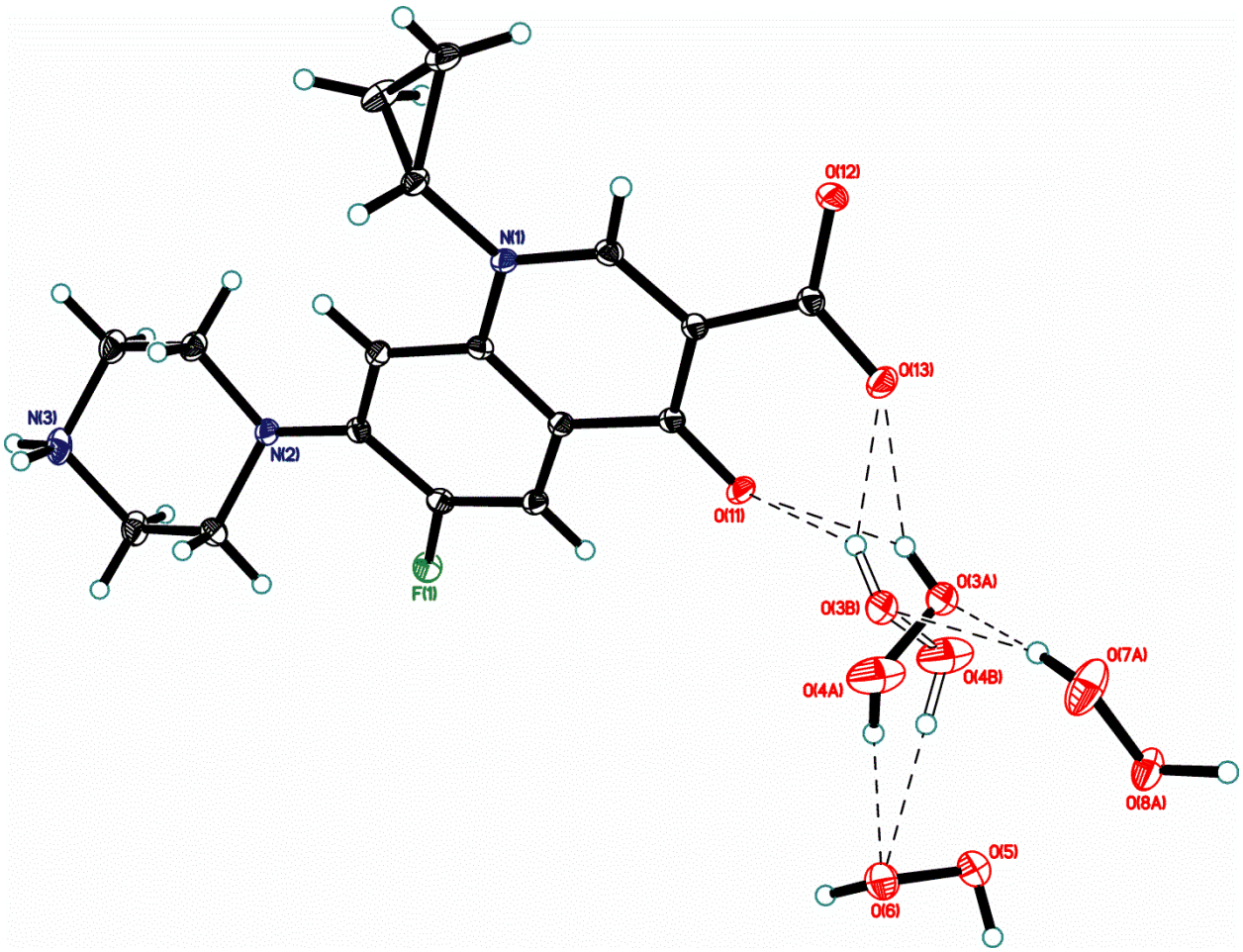

Figure S2 Hydrogen bonds (dashed lines) formed by peroxide molecule H3-O3-O4-H4 in **2**. Minor component of disorder is shown as open lines.

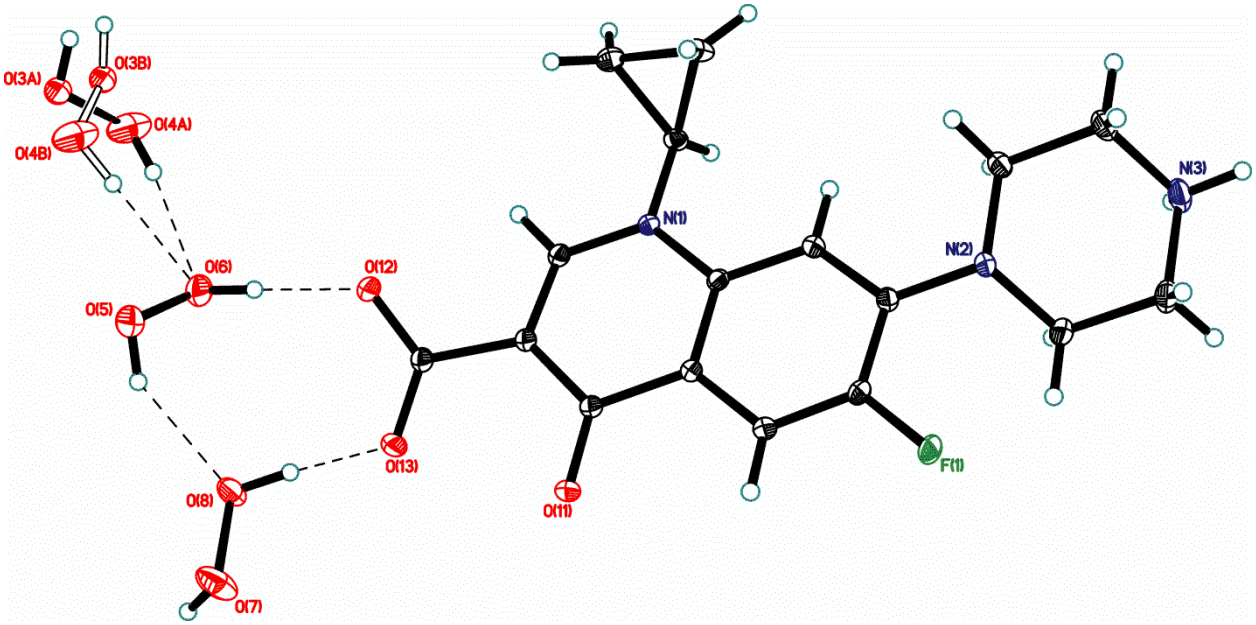

Figure S3 Hydrogen bonds (dashed lines) formed by peroxide molecule H5-O5-O6-H6 in **2**.

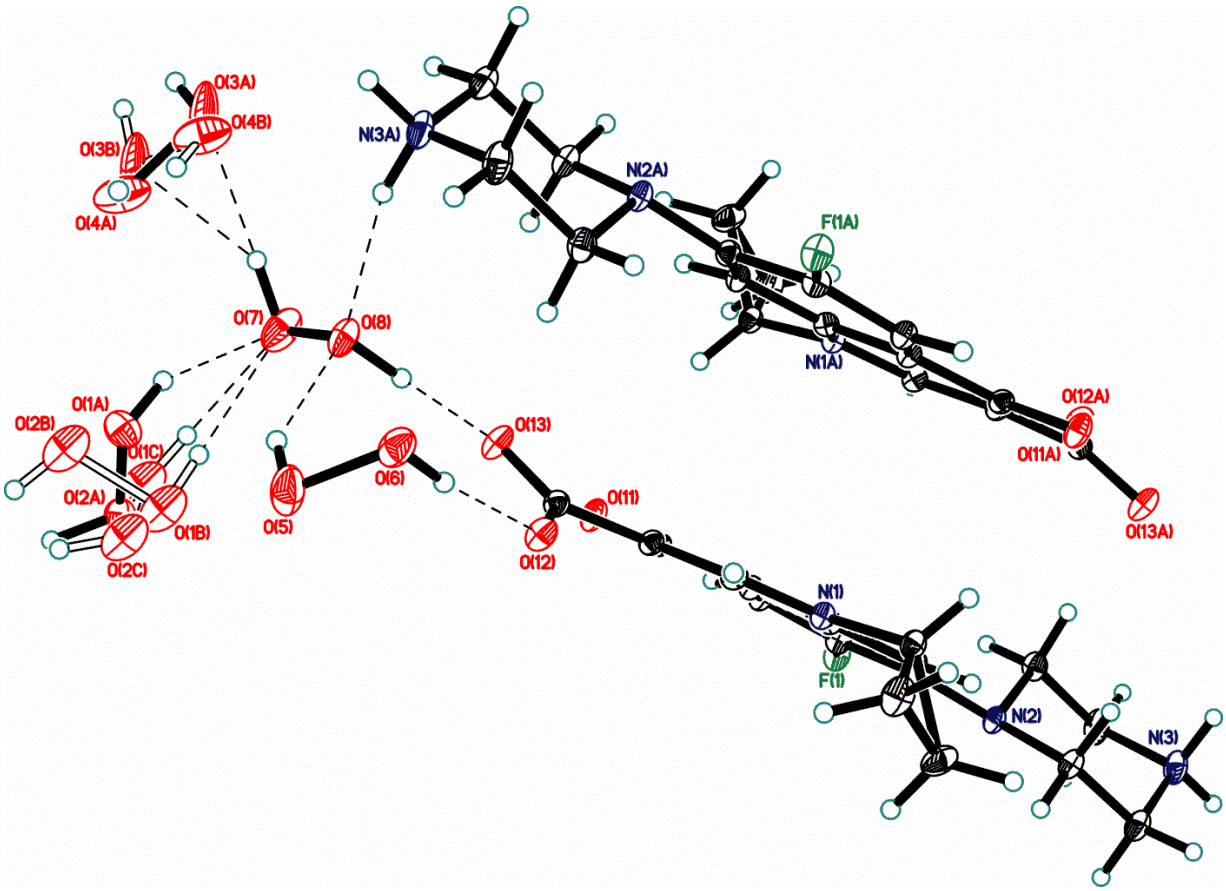

Figure S4 Hydrogen bonds (dashed lines) formed by peroxide molecule H7-O7-O8-H8 in **2**.

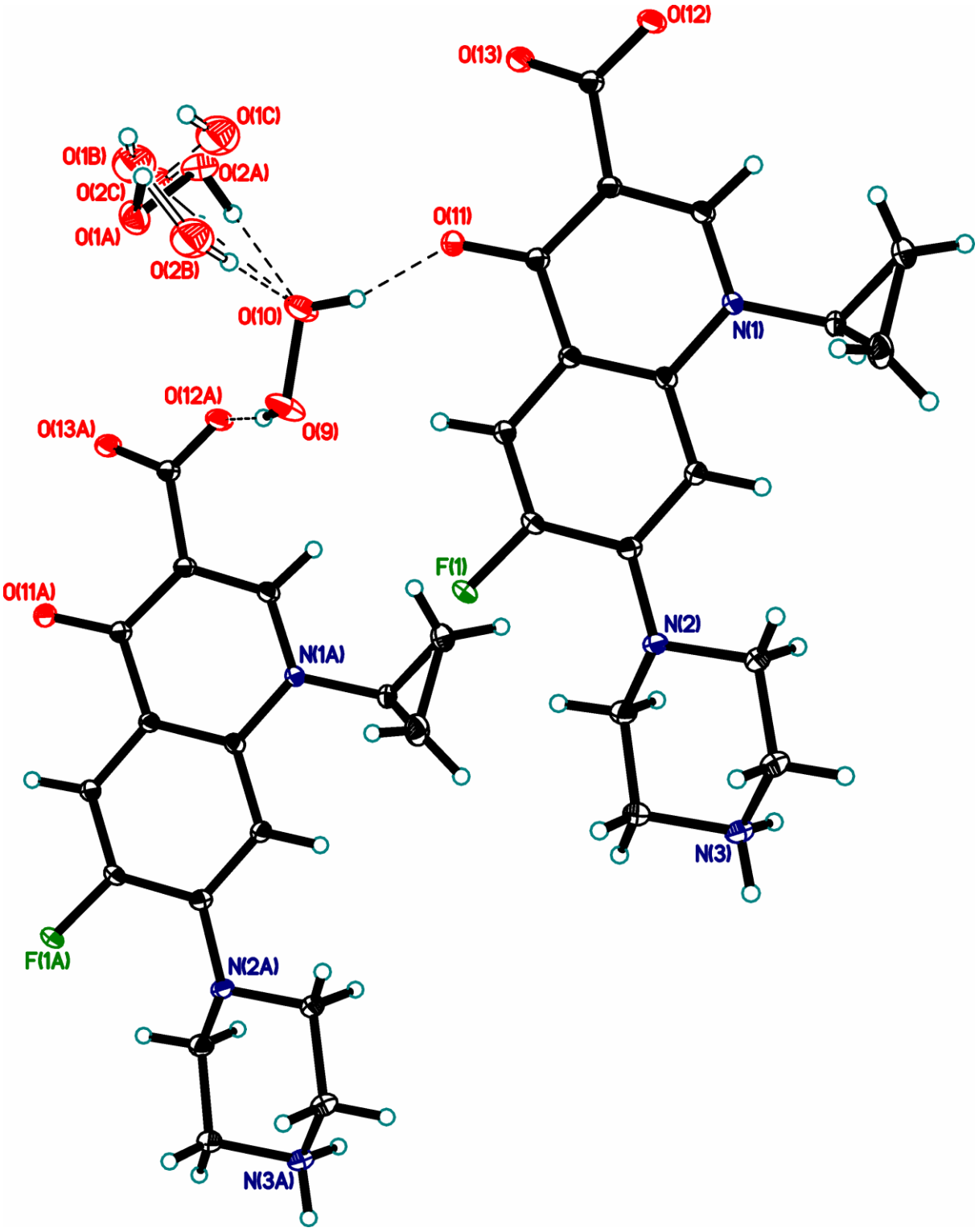

Figure S5 Hydrogen bonds (dashed lines) formed by peroxide molecule H9-O9-O10-H10 in **2**.

Table S1. Geometric parameters of hydrogen bonds in the structure **1**.

D–H…A	D–H, Å	H…A, Å	D…A, Å	∠ D–H…A, °
O3–H1…O1	0.95(2)	1.65(2)	2.5447(13)	156(2)
O4–H4…O1	0.90(2)	1.93(2)	2.8040(12)	165.0(17)
O5–H5…O2*	0.88(2)	1.91(2)	2.7837(13)	172(2)

* Symmetry operation: 1-x, 1-y, 2-z

Table S2. Geometric parameters of hydrogen bonds in the structure **2**.

D–H…A	D–H, Å	H…A, Å	D…A, Å	∠ D–H…A, °
O1A–H1A…O7[1]	0.95(4)	1.75(4)	2.624(2)	152(4)
O1B–H1B…O7[1]	0.85	2.02	2.865(6)	179.9
O1C–H1C…O7[1]	0.85	1.84	2.694(9)	178.2
O2A–H2A…O10[2]	0.92(4)	1.82(4)	2.732(2)	172(4)
O2B–H2B…O10[2]	0.85	1.73	2.582(6)	179.7
O2C–H2C…O10[2]	0.85	1.98	2.827(9)	178.7
O3A–H3A…O11	0.76(3)	2.31(3)	2.9174(18)	138(3)
O3A–H3A…O13	0.76(3)	2.13(3)	2.7794(17)	144(3)
O4A–H4A…O6[3]	0.89(3)	1.88(3)	2.7304(17)	158(2)
O3B–H3B…O11	0.85	2.20	2.903(13)	140.1
O3B–H3B…O13	0.85	1.95	2.616(11)	134.7
O4B–H4B…O6[3]	0.85	1.96	2.809(12)	179.7
O5–H5…O8	0.86(3)	2.11(3)	2.8729(15)	148(2)
O6–H6…O12	0.92(2)	1.76(2)	2.6821(13)	173(2)
O7–H7…O3A[1]	0.96(4)	1.99(4)	2.956(2)	175(3)
O7–H7…O3B[1]	0.96(4)	1.94(4)	2.789(12)	146(3)
O8–H8…O13	0.95(2)	1.63(2)	2.5730(13)	176(2)
O9–H9…O12[3]	0.86(2)	1.87(2)	2.7188(14)	171(2)
O10–H10…O11	0.94(3)	1.73(3)	2.6445(13)	162(2)
N3–H31…O2A[4]	0.90(2)	1.99(2)	2.841(2)	158.6(19)
N3–H31…O1B[4]	0.90(2)	1.94(2)	2.772(5)	152.8(19)
N3–H31…O2C[4]	0.90(2)	1.87(2)	2.763(8)	170(2)
N3–H32…O8[5]	0.94(2)	2.02(2)	2.9419(16)	165.2(17)

Symmetry operations: (1) 1-x, 1-y, 2-z; (2) -1+x, y, z; (3) x, -1+y, z; (4) 1+x, y, -1+z; (5) 1-x, 1-y, 1-z.

Experimental details.

Nalidixic acid and ciprofloxacin were obtained from LLC "Sputnik-K" (Russia) and Sigma-Aldrich, respectively. 60 wt% hydrogen peroxide was purchased from Fisher Scientific (Loughborough, UK). 96 wt% hydrogen peroxide was prepared by an evaporation method.[S1] Handling procedures for concentrated hydrogen peroxide are described in detail (danger of explosion!). [S2, S3]

Colourless crystals of **1** and **2** were obtained by cooling to −21°C saturated solutions (rt) of respective organic coformers in 96 wt% hydrogen peroxide. Unfortunately, both crystalline samples were unstable without mother liquors. The latter prevented carrying-out powder diffraction and DSC experiments.

The samples were withdrawn from the crystallization vials using corrosion-resistant steel spatula and immediately placed inside a drop of perfluorinated Fomblin YR-1800 oil on the microscope slides. The appropriate single crystals were mounted on the top of MiTeGen MicroMeshes and transferred instantly to a cold nitrogen stream on the diffractometer.

Experimental data sets were collected on a Bruker D8 Venture machine using graphite monochromatized Mo-*K*α radiation (λ = 0.71073 Å). Absorption corrections based on measurements of equivalent reflections were applied. [S4] The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. [S5] In the structure **2**, two of five independent peroxide molecules were disordered over two or three positions with occupancy ratios 0.883(2)/0.117(2) and 0.539(3)/0.279(2)/0.182(2). All hydrogen atoms (except for disordered H_2O_2 molecules in **2**) were found from difference Fourier synthesis and refined with isotropic thermal parameters. Hydrogen atoms of disordered peroxide species were placed on the lines connecting hydrogen bonded oxygen atoms at distances 0.85 Å from O_{peroxo} positions and they were refined using a riding model (AFIX 3) with $U_{iso}(H)=1.5\times U_{eq}(O)$. Details of X-ray studies are listed in Table S3. The single-crystal X-ray diffraction experiments were performed at the Centre of Shared Equipment of IGIC RAS. Crystallographic data deposited with Cambridge Structural Database under the numbers 2292623 and 2292624.

S1. M. V. Vener, A. V. Churakov, A. P. Voronin, O. D. Parashchuk, S. V. Artobolevskii, O. A. Alatortsev, D. E. Makhrov, A. G. Medvedev and A. Filarowski, *Molecules*, 2022, **27**, 717.

S2. W. C. Schumb, C. N. Satterfield and R. P. Wentworth, *Hydrogen Peroxide,* Reinhold Publishing, New York, 1955.

S3. O. Maass and W. H. Hatcher, *J. Am. Chem. Soc.*, 1920, **42**, 2548.

S4. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.

S5. G. M. Sheldrick, *Acta Crystallogr.,* 2015, **C71**, 3.

Table S3. Crystal data and details of X-ray analysis for **1** and **2**.

	1	**2**
Formula	$C_{12}H_{14}N_2O_5$	$C_{17}H_{28}F_1N_3O_{13}$
*F*w	266.25	501.42
colour, habit	colourless, plate	colourless, prism
crystal size (mm)	0.30×0.15×0.02	0.20×0.17×0.07
temperature (K)	150	100
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	7.1035(4)	7.6295(3)
b (Å)	9.6341(6)	9.4504(4)
c (Å)	9.9683(6)	14.5004(6)
α (deg)	106.911(2)	90.7960(12)
β (deg)	104.324(2)	97.0169(14)
γ (deg)	102.288(2)	90.1787(14)
V (Å^3)	601.82(6)	1037.56(7)
Z	2	2
D_c (g·cm^{-3})	1.469	1.605
μ (mm^{-1})	0.116	0.144
F(000)	280	528
θ range (deg)	2.26 to 29.00	2.16 to 30.00
reflections collected	8755	17079
unique reflections / R_{int}	3198 / 0.0215	6043 / 0.0220
reflections with $I>2\sigma(I)$	2720	5299
No of parameters	228	447
GooF on F^2	1.076	1.029
R_1 ($I>2\sigma(I)$)	0.0409	0.0436
wR_2(all data)	0.1039	0.1122
largest diff peak / hole (e·Å^{-3})	0.34 / -0.21	0.59 / -0.64