Electronic Supporting Information (ESI)

MONOSULFONATED DIBENZO-24-CROWN-8 AND ITS PROPERTIES

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Table 1S. Crystal data and structure refinement details for investigated compounds.

Compound	**SDB24C8⁻K⁺**	**SDB24C8⁻H₃O⁺**
Empirical formula	$C_{24}H_{35}KO_{13}S$	$C_{24}H_{34}O_{12}S$
Formula weight	602.68	546.57
Temperature/K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	9.5640(5)	9.3346(4)
b/Å	11.4132(5)	11.4965(5)
c/Å	14.4900(7)	14.0008(5)
α/°	89.466(4)	68.283(4)
β/°	70.873(5)	88.338(3)
γ/°	66.708(5)	66.351(4)
Volume/Å^3	1359.32(13)	1265.99(10)
Z	2	2
ρ_{calc}g/cm^3	1.472	1.434
μ/mm^{-1}	3.017	1.706
F(000)	636.0	580.0
Crystal size/mm^3	0.28 × 0.17 × 0.15	0.50 × 0.14 × 0.14
Radiation	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)
2Θ range for data collection/°	6.52 to 134.134	6.864 to 134.118
Index ranges	$-9 \le h \le 11$, $-10 \le k \le 13$, $-16 \le l \le 17$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-16 \le l \le 16$
Reflections collected	8668	17259
Independent reflections	4847 [R_{int} = 0.0204, R_{sigma} = 0.0278]	4517 [R_{int} = 0.0248, R_{sigma} = 0.0179]
Data/restraints/parameters	4847/6/387	4517/17/439
Goodness-of-fit on F^2	1.030	1.027
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0798	R_1 = 0.0421, wR_2 = 0.1080
Final *R* indexes [all data]	R_1 = 0.0329, wR_2 = 0.0817	R_1 = 0.0439, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.36/-0.48	0.40/-0.49

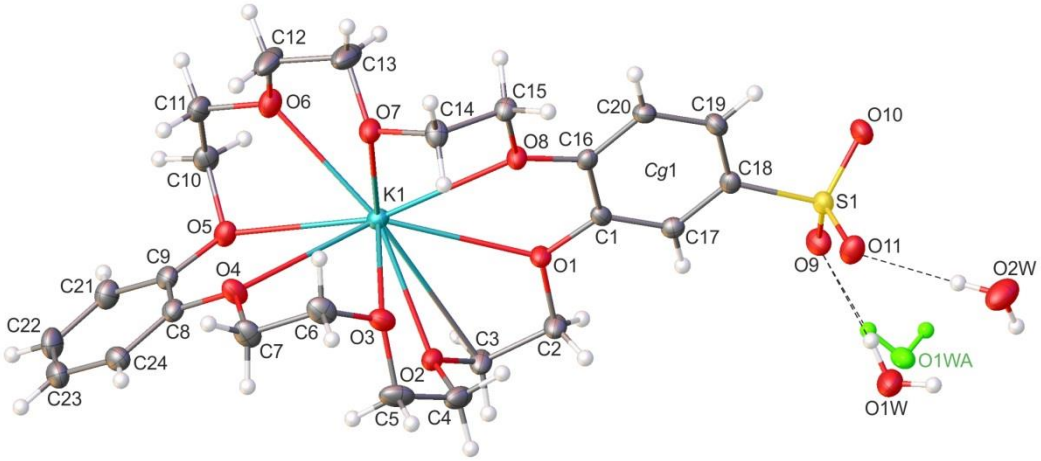

Figure 1S. Asymmetric unit of the crystal lattice of **SDB24C8⁻K⁺**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius. The hydrogen bonds are represented by dashed lines. Minor parts of the disordered fragments are coloured in green. *Cg*1 denotes the geometric centre of gravity of the aromatic ring delineated by the C1/C16/C20–C17 atoms.

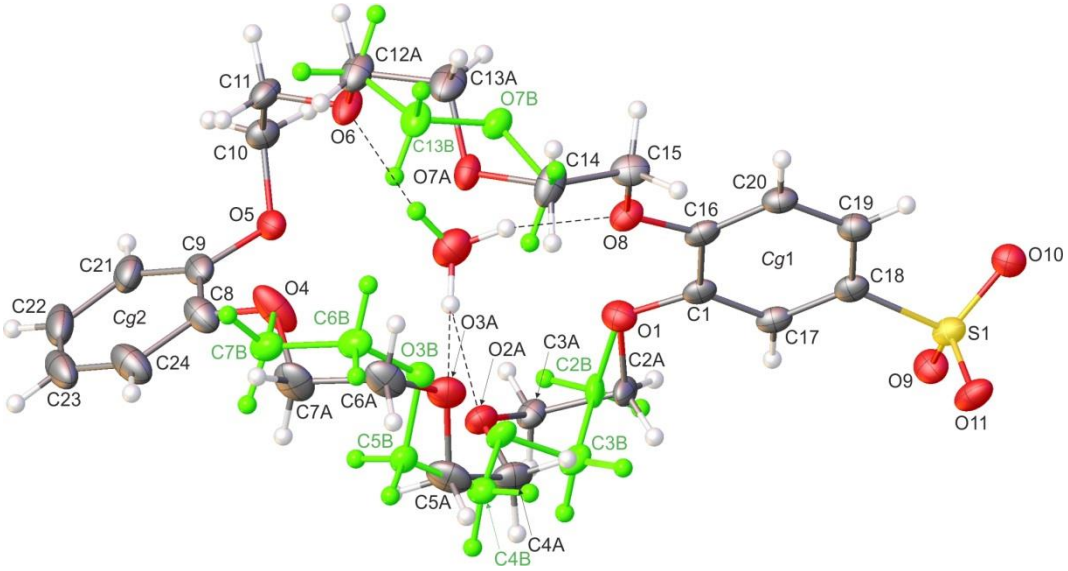

Figure 2S. Asymmetric unit of the crystal lattice of **SDB24C8⁻H₃O⁺**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius. The hydrogen bonds are represented by dashed lines. Minor parts of the disordered fragments are coloured in green. *Cg*1 and *Cg*2 denote the geometric centers of gravity of the aromatic rings delineated by the C1/C16/C20–C17 and C8–C9/C21–C24 atoms, respectively.

Table 2S. Bond lengths for **SDB24C8^{-}K^{+}**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C16	1.408(2)	C16	C20	1.385(2)
C1	C17	1.388(2)	C16	O8	1.3673(18)
C1	O1	1.3665(18)	C17	C18	1.393(2)
C2	C3	1.508(2)	C18	C19	1.381(2)
C2	O1	1.4324(18)	C18	S1	1.7741(15)
C3	K1	3.5027(16)	C19	C20	1.396(2)
C3	O2	1.425(2)	C21	C22	1.391(3)
C4	C5	1.497(3)	C22	C23	1.379(3)
C4	O2	1.416(2)	C23	C24	1.391(2)
C5	O3	1.434(2)	K1	O1	3.0677(11)
C6	C7	1.510(2)	K1	O2	2.7363(11)
C6	O3	1.423(2)	K1	O3	2.8187(11)
C7	O4	1.4359(19)	K1	O4	3.1664(11)
C8	C9	1.400(2)	K1	O5	2.9867(11)
C8	C24	1.391(2)	K1	O6	2.8556(12)
C8	O4	1.3716(19)	K1	O7	2.8192(11)
C9	C21	1.385(2)	K1	O8	3.0064(11)
C9	O5	1.3828(19)	K1	O9^{1}	2.8063(12)
C10	C11	1.498(2)	K1	O10^{1}	2.9594(12)
C10	O5	1.4425(19)	K1	S1^{1}	3.4129(5)
C11	O6	1.4247(19)	O9	K1^{1}	2.8062(12)
C12	C13	1.506(3)	O9	S1	1.4627(12)
C12	O6	1.415(2)	O10	K1^{1}	2.9593(12)
C13	O7	1.426(2)	O10	S1	1.4527(12)
C14	C15	1.503(2)	O11	S1	1.4621(12)
C14	O7	1.4247(18)	S1	K1^{1}	3.4129(5)
C15	O8	1.4388(18)			

^{1}1-X,-Y,1-Z

Table 3S. Values of valence angles for **SDB24C8^{-}K^{+}**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	C1	C16	120.01(13)	O6	K1	O5	58.79(3)
O1	C1	C16	115.52(13)	O6	K1	O8	104.88(3)
O1	C1	C17	124.46(13)	O6	K1	O10^{1}	97.19(3)
O1	C2	C3	106.55(12)	O6	K1	S1^{1}	88.79(3)
C2	C3	K1	94.96(9)	O7	K1	C3	142.08(4)
O2	C3	C2	113.34(13)	O7	K1	O1	109.25(3)
O2	C3	K1	46.96(7)	O7	K1	O4	81.62(3)
O2	C4	C5	107.27(13)	O7	K1	O5	108.71(3)
O3	C5	C4	108.78(14)	O7	K1	O6	58.11(3)
O3	C6	C7	114.07(14)	O7	K1	O8	59.51(3)
O4	C7	C6	107.96(13)	O7	K1	O10^{1}	145.79(3)
C24	C8	C9	119.42(15)	O7	K1	S1^{1}	123.00(3)
O4	C8	C9	116.14(14)	O8	K1	C3	90.17(3)
O4	C8	C24	124.44(15)	O8	K1	O1	50.49(3)
C21	C9	C8	119.90(15)	O8	K1	O4	131.14(3)
O5	C9	C8	117.98(13)	O8	K1	S1^{1}	92.71(2)
O5	C9	C21	121.93(14)	O9^{1}	K1	C3	94.82(4)

O5	C10	C11	111.56(13)	O9[1]	K1	O1	74.84(3)
O6	C11	C10	108.35(13)	O9[1]	K1	O3	158.96(4)
O6	C12	C13	108.42(16)	O9[1]	K1	O4	143.55(3)
O7	C13	C12	107.34(15)	O9[1]	K1	O5	96.01(3)
O7	C14	C15	115.18(13)	O9[1]	K1	O6	76.35(3)
O8	C15	C14	108.21(12)	O9[1]	K1	O7	98.41(3)
C20	C16	C1	119.70(14)	O9[1]	K1	O8	75.59(3)
O8	C16	C1	115.64(13)	O9[1]	K1	O10[1]	49.66(3)
O8	C16	C20	124.59(14)	O9[1]	K1	S1[1]	24.84(2)
C1	C17	C18	119.46(14)	O10[1]	K1	C3	63.92(4)
C17	C18	S1	119.70(12)	O10[1]	K1	O1	77.28(3)
C19	C18	C17	120.78(14)	O10[1]	K1	O4	115.70(3)
C19	C18	S1	119.39(12)	O10[1]	K1	O5	69.29(3)
C18	C19	C20	119.89(14)	O10[1]	K1	O8	113.00(3)
C16	C20	C19	120.01(14)	O10[1]	K1	S1[1]	25.08(2)
C9	C21	C22	120.49(16)	S1[1]	K1	C3	76.79(3)
C23	C22	C21	119.58(16)	C1	O1	C2	116.63(12)
C22	C23	C24	120.60(16)	C1	O1	K1	126.13(8)
C23	C24	C8	120.01(16)	C2	O1	K1	117.05(8)
O1	K1	C3	41.39(3)	C3	O2	K1	110.66(9)
O1	K1	O4	139.84(3)	C4	O2	C3	115.03(13)
O1	K1	S1[1]	72.01(2)	C4	O2	K1	117.19(9)
O2	K1	C3	22.37(4)	C5	O3	K1	115.57(9)
O2	K1	O1	55.07(3)	C6	O3	C5	114.25(13)
O2	K1	O3	59.65(3)	C6	O3	K1	112.79(9)
O2	K1	O4	87.87(3)	C7	O4	K1	115.42(9)
O2	K1	O5	101.28(3)	C8	O4	C7	116.48(12)
O2	K1	O6	158.27(3)	C8	O4	K1	122.88(9)
O2	K1	O7	130.20(3)	C9	O5	C10	115.84(12)
O2	K1	O8	95.34(3)	C9	O5	K1	128.78(9)
O2	K1	O9[1]	117.19(3)	C10	O5	K1	103.59(9)
O2	K1	O10[1]	81.82(3)	C11	O6	K1	120.64(9)
O2	K1	S1[1]	98.28(3)	C12	O6	C11	112.69(13)
O3	K1	C3	80.51(4)	C12	O6	K1	119.29(10)
O3	K1	O1	88.65(3)	C13	O7	K1	111.89(11)
O3	K1	O4	56.19(3)	C14	O7	C13	113.32(13)
O3	K1	O5	105.02(3)	C14	O7	K1	112.49(9)
O3	K1	O6	114.06(4)	C15	O8	K1	115.45(8)
O3	K1	O7	74.48(3)	C16	O8	C15	115.87(11)
O3	K1	O8	83.88(3)	C16	O8	K1	127.47(9)
O3	K1	O10[1]	139.72(3)	S1	O9	K1[1]	101.48(6)
O3	K1	S1[1]	157.03(3)	S1	O10	K1[1]	95.21(5)
O4	K1	C3	107.45(4)	C18	S1	K1[1]	111.87(5)
O4	K1	S1[1]	135.13(2)	O9	S1	C18	105.74(7)
O5	K1	C3	104.99(4)	O9	S1	K1[1]	53.69(5)
O5	K1	O1	141.85(3)	O10	S1	C18	106.82(7)
O5	K1	O4	51.00(3)	O10	S1	K1[1]	59.71(5)
O5	K1	O8	163.38(3)	O10	S1	O9	112.58(7)
O5	K1	S1[1]	84.35(2)	O10	S1	O11	112.90(7)
O6	K1	C3	159.71(4)	O11	S1	C18	105.56(7)
O6	K1	O1	146.09(3)	O11	S1	K1[1]	142.38(5)

O6	K1	O4	72.92(3)	O11	S1	O9	112.53(7)

[1]1-X,-Y,1-Z

Table 4S. Values of torsion angles for **SDB24C8⁻K⁺**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C16	C20	C19	-3.4(2)	C17	C18	C19	C20	2.9(2)
C1	C16	O8	C15	169.99(12)	C17	C18	S1	K1[1]	83.61(12)
C1	C16	O8	K1	-23.29(17)	C17	C18	S1	O9	26.96(14)
C1	C17	C18	C19	-2.0(2)	C17	C18	S1	O10	147.10(12)
C1	C17	C18	S1	173.86(11)	C17	C18	S1	O11	-92.49(13)
C2	C3	O2	C4	-61.55(18)	C18	C19	C20	C16	-0.2(2)
C2	C3	O2	K1	74.10(15)	C19	C18	S1	K1[1]	-100.51(12)
C3	C2	O1	C1	177.49(13)	C19	C18	S1	O9	-157.16(12)
C3	C2	O1	K1	2.25(16)	C19	C18	S1	O10	-37.03(14)
C4	C5	O3	C6	176.60(13)	C19	C18	S1	O11	83.38(13)
C4	C5	O3	K1	43.26(16)	C20	C16	O8	C15	-6.8(2)
C5	C4	O2	C3	-174.01(13)	C20	C16	O8	K1	159.96(11)
C5	C4	O2	K1	53.32(15)	C21	C9	O5	C10	61.4(2)
C6	C7	O4	C8	173.64(13)	C21	C9	O5	K1	-162.27(12)
C6	C7	O4	K1	18.39(16)	C21	C22	C23	C24	-0.7(3)
C7	C6	O3	C5	-64.74(18)	C22	C23	C24	C8	0.2(3)
C7	C6	O3	K1	69.90(14)	C24	C8	C9	C21	-0.8(2)
C8	C9	C21	C22	0.3(3)	C24	C8	C9	O5	-175.94(14)
C8	C9	O5	C10	-123.62(15)	C24	C8	O4	C7	9.5(2)
C8	C9	O5	K1	12.75(19)	C24	C8	O4	K1	162.75(12)
C9	C8	C24	C23	0.6(2)	K1	C3	O2	C4	-135.65(14)
C9	C8	O4	C7	-170.34(14)	K1[1]	O9	S1	C18	105.85(6)
C9	C8	O4	K1	-17.10(18)	K1[1]	O9	S1	O10	-10.44(8)
C9	C21	C22	C23	0.5(3)	K1[1]	O9	S1	O11	-139.40(6)
C10	C11	O6	C12	-176.01(15)	K1[1]	O10	S1	C18	-105.90(6)
C10	C11	O6	K1	-26.23(17)	K1[1]	O10	S1	O9	9.74(7)
C11	C10	O5	C9	80.48(16)	K1[1]	O10	S1	O11	138.51(6)
C11	C10	O5	K1	-65.93(13)	O1	C1	C16	C20	-177.10(13)
C12	C13	O7	C14	-168.05(16)	O1	C1	C16	O8	5.98(18)
C12	C13	O7	K1	63.48(19)	O1	C1	C17	C18	179.89(13)
C13	C12	O6	C11	-178.42(16)	O1	C2	C3	K1	-1.76(12)
C13	C12	O6	K1	31.4(2)	O1	C2	C3	O2	-46.64(18)
C14	C15	O8	C16	-159.98(12)	O2	C4	C5	O3	-62.54(17)
C14	C15	O8	K1	31.66(14)	O3	C6	C7	O4	-57.00(18)
C15	C14	O7	C13	-69.52(19)	O4	C8	C9	C21	179.05(14)
C15	C14	O7	K1	58.65(15)	O4	C8	C9	O5	3.9(2)
C16	C1	C17	C18	-1.6(2)	O4	C8	C24	C23	-179.26(15)
C16	C1	O1	C2	-162.19(13)	O5	C9	C21	C22	175.22(15)
C16	C1	O1	K1	12.57(17)	O5	C10	C11	O6	65.07(17)
C17	C1	C16	C20	4.3(2)	O6	C12	C13	O7	-62.0(2)
C17	C1	C16	O8	-172.64(12)	O7	C14	C15	O8	-61.31(17)
C17	C1	O1	C2	16.4(2)	O8	C16	C20	C19	173.25(13)
C17	C1	O1	K1	-168.88(10)	S1	C18	C19	C20	-172.96(12)

[1]1-X,-Y,1-Z

Table 5S. Bond lengths for **SDB24C8⁻H₃O⁺**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C16	1.404(2)	C9	O5	1.390(2)
C1	C17	1.386(3)	C10	C11	1.499(3)
C1	O1	1.377(2)	C10	O5	1.436(2)
C2A	C3A	1.536(2)	C11	O6	1.420(2)
C2A	O1	1.446(9)	C12	C13A	1.494(5)
C2B	C3B	1.505(9)	C12	C13B	1.464(5)
C2B	O1	1.448(10)	C12	O6	1.413(2)
C3A	O2A	1.429(4)	C13A	O7A	1.436(6)
C3B	O2B	1.439(5)	C13B	O7B	1.436(7)
C4A	C5A	1.513(8)	C14	C15	1.479(3)
C4A	O2A	1.411(6)	C14	O7A	1.431(3)
C4B	C5B	1.509(6)	C14	O7B	1.467(4)
C4B	O2B	1.404(9)	C15	O8	1.438(2)
C5A	O3A	1.426(8)	C16	C20	1.387(3)
C5B	O3B	1.427(6)	C16	O8	1.369(2)
C6A	C7A	1.510(7)	C17	C18	1.392(3)
C6A	O3A	1.420(7)	C18	C19	1.384(3)
C6B	C7B	1.495(7)	C18	S1	1.7790(19)
C6B	O3B	1.441(6)	C19	C20	1.394(3)
C7A	O4	1.561(5)	C21	C22	1.396(3)
C7B	O4	1.382(5)	C22	C23	1.366(4)
C8	C9	1.393(3)	C23	C24	1.388(4)
C8	C24	1.399(3)	O9	S1	1.4568(13)
C8	O4	1.368(3)	O10	S1	1.4595(14)
C9	C21	1.386(3)	O11	S1	1.4578(14)

Table 6S. Values of valence angles for **SDB24C8⁻H₃O⁺**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	C1	C16	120.37(17)	O8	C16	C1	116.29(17)
O1	C1	C16	114.94(16)	O8	C16	C20	124.17(16)
O1	C1	C17	124.69(16)	C1	C17	C18	119.50(16)
O1	C2A	C3A	102.8(4)	C17	C18	S1	120.98(14)
O1	C2B	C3B	107.2(6)	C19	C18	C17	120.33(17)
O2A	C3A	C2A	114.4(4)	C19	C18	S1	118.52(15)
O2B	C3B	C2B	108.1(4)	C18	C19	C20	120.22(18)
O2A	C4A	C5A	107.1(5)	C16	C20	C19	119.90(17)
O2B	C4B	C5B	108.6(5)	C9	C21	C22	120.3(2)
O3A	C5A	C4A	107.1(5)	C23	C22	C21	119.9(2)
O3B	C5B	C4B	108.0(5)	C22	C23	C24	120.4(2)
O3A	C6A	C7A	114.7(5)	C23	C24	C8	120.4(2)
O3B	C6B	C7B	115.1(4)	C1	O1	C2A	109.3(2)
C6A	C7A	O4	111.6(3)	C1	O1	C2B	128.1(3)
O4	C7B	C6B	103.7(4)	C4A	O2A	C3A	115.0(3)
C9	C8	C24	119.0(2)	C4B	O2B	C3B	113.0(4)
O4	C8	C9	116.50(17)	C6A	O3A	C5A	114.7(5)
O4	C8	C24	124.5(2)	C5B	O3B	C6B	112.8(4)
C21	C9	C8	119.97(19)	C8	O4	C7A	117.5(2)
C21	C9	O5	121.17(19)	C8	O4	C7B	112.1(2)
O5	C9	C8	118.67(17)	C9	O5	C10	115.50(14)
O5	C10	C11	112.56(15)	C12	O6	C11	113.17(14)

O6	C11	C10	107.93(15)	C14	O7A	C13A	109.4(3)
O6	C12	C13A	106.6(2)	C13B	O7B	C14	108.4(4)
O6	C12	C13B	114.5(2)	C16	O8	C15	116.89(14)
O7A	C13A	C12	108.3(4)	O9	S1	C18	106.20(8)
O7B	C13B	C12	109.2(4)	O9	S1	O10	112.78(8)
O7A	C14	C15	124.1(2)	O9	S1	O11	113.86(8)
O7B	C14	C15	97.7(2)	O10	S1	C18	106.19(8)
O8	C15	C14	109.29(16)	O11	S1	C18	105.10(8)
C20	C16	C1	119.51(17)	O11	S1	O10	111.92(8)

Table 7S. Values of torsion angles for **SDB24C8⁻H$_3$O$^+$**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C16	C20	C19	-3.2(3)	C17	C1	O1	C2B	20.4(5)
C1	C16	O8	C15	167.52(15)	C17	C18	C19	C20	3.1(3)
C1	C17	C18	C19	-2.2(3)	C17	C18	S1	O9	25.79(16)
C1	C17	C18	S1	172.97(13)	C17	C18	S1	O10	146.06(14)
C2A	C3A	O2A	C4A	-55.7(5)	C17	C18	S1	O11	-95.19(15)
C2B	C3B	O2B	C4B	-174.0(6)	C18	C19	C20	C16	-0.4(3)
C3A	C2A	O1	C1	175.7(3)	C19	C18	S1	O9	-158.94(14)
C3B	C2B	O1	C1	91.6(4)	C19	C18	S1	O10	-38.66(16)
C4A	C5A	O3A	C6A	175.4(5)	C19	C18	S1	O11	80.09(16)
C4B	C5B	O3B	C6B	-170.3(5)	C20	C16	O8	C15	-10.5(2)
C5A	C4A	O2A	C3A	-177.7(4)	C21	C9	O5	C10	69.7(2)
C5B	C4B	O2B	C3B	-179.4(4)	C21	C22	C23	C24	0.2(3)
C6A	C7A	O4	C8	165.2(4)	C22	C23	C24	C8	-1.7(3)
C6B	C7B	O4	C8	172.7(3)	C24	C8	C9	C21	-0.7(3)
C7A	C6A	O3A	C5A	-69.5(6)	C24	C8	C9	O5	-175.80(18)
C7B	C6B	O3B	C5B	-54.6(5)	C24	C8	O4	C7A	21.5(4)
C8	C9	C21	C22	-0.7(3)	C24	C8	O4	C7B	-9.2(4)
C8	C9	O5	C10	-115.32(19)	O1	C1	C16	C20	-175.36(15)
C9	C8	C24	C23	2.0(3)	O1	C1	C16	O8	6.5(2)
C9	C8	O4	C7A	-157.3(3)	O1	C1	C17	C18	178.00(15)
C9	C8	O4	C7B	172.0(3)	O1	C2A	C3A	O2A	-51.9(6)
C9	C21	C22	C23	1.0(3)	O1	C2B	C3B	O2B	66.0(5)
C10	C11	O6	C12	-178.67(17)	O2A	C4A	C5A	O3A	-61.3(6)
C11	C10	O5	C9	76.7(2)	O2B	C4B	C5B	O3B	-58.1(6)
C12	C13A	O7A	C14	-171.1(3)	O3A	C6A	C7A	O4	-63.5(6)
C12	C13B	O7B	C14	-168.5(3)	O3B	C6B	C7B	O4	-50.1(5)
C13A	C12	O6	C11	-174.6(3)	O4	C8	C9	C21	178.13(18)
C13B	C12	O6	C11	148.2(3)	O4	C8	C9	O5	3.1(3)
C14	C15	O8	C16	-158.44(16)	O4	C8	C24	C23	-176.8(2)
C15	C14	O7A	C13A	-77.9(4)	O5	C9	C21	C22	174.20(18)
C15	C14	O7B	C13B	-174.2(3)	O5	C10	C11	O6	66.0(2)
C16	C1	C17	C18	-1.4(3)	O6	C12	C13A	O7A	-62.2(4)
C16	C1	O1	C2A	-164.6(4)	O6	C12	C13B	O7B	56.4(5)
C16	C1	O1	C2B	-160.2(4)	O7A	C14	C15	O8	-51.6(3)
C17	C1	C16	C20	4.0(3)	O7B	C14	C15	O8	-79.4(2)
C17	C1	C16	O8	-174.06(15)	O8	C16	C20	C19	174.78(16)
C17	C1	O1	C2A	16.0(4)	S1	C18	C19	C20	-172.21(14)

Table 8S. Parameters describing selected geometrical features of **S**DB24C8⁻K⁺, **S**DB24C8⁻H_3O^+ and [K(DB24C8)(DME)]$_2C_{60}$·DME.*

Geometrical parameter [Å, °]		**SDB24C8⁻K⁺**	**SDB24C8⁻H_3O^+**	**[K(DB24C8)(DME)]$_2C_{60}$·DME**
	d(*Cg*1···*Cg*2)	10.24(2)	10.23(2)	9.59(2)
d(*Cg*I···*Cg*J)	**d(*Cg*1···*Cg*1^i)**	4.43(2)	4.31(2)	–
	d(*Cg*2···*Cg*2^i)	19.42(2)	19.53(2)	–
	<(*Cg*1···*Cg*2)	74.04(6)	72.54(7)	51.04(15)
<(*Cg*I···*Cg*J)	**<(*Cg*1···*Cg*1^i)**	0.0(4)	0.0(4)	–
	<(*Cg*1···*Cg*1^i)	0.0(2)	0.0(4)	–

Where: d(*Cg*I···*Cg*J) and <(*Cg*I···*Cg*J) – distance between the centers of gravity and the angle between planes of the phenyl rings within the DB24C8 moiety and the [K(**S**DB24C8)]$_2$ / [H_3O(**S**DB24C8)]$_2$ assemblies (see Fig. 1). Symmetry codes: (i) (**S**DB24C8⁻K⁺) $-x + 1, -y, -z + 1$; (i) (**S**DB24C8⁻H_3O^+) $-x + 1, -y + 2, -z + 1$.

*Data for [K(DB24C8)(DME)]$_2C_{60}$·DME sourced from N. V. Kozhemyakina et al., *Eur. J. Inorg. Chem.*, 2009, 3900–3903.

Table 9S. Geometrical parameters of hydrogen bonds in the crystal of **SDB24C8⁻K⁺**.

D–H···A	**D–H [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(D–H···A) [°]**
O2W–H2WA···O11	0.85(3)	2.01(3)	2.852(2)	172(3)
O2W–H2WB···O1W^{ii}	0.88(3)	1.93(3)	2.805(7)	173(3)
O2W–H2WB···O1WA^{ii}	0.88(3)	1.96(3)	2.808(8)	163(3)
O1W–H1WA···O1W^{ii}	0.84(5)	1.99(5)	2.828(13)	176(5)
O1W–H1WA···O1WA^{ii}	0.84(5)	2.01(5)	2.818(12)	164(4)
O1W–H1WB···O9	0.85(3)	2.01(3)	2.846(6)	171(7)
C15–H15A···O2W^{iii}	0.97	2.42	3.053(2)	122
C22–H22···O1W^{iv}	0.93	2.58	3.261(13)	130

Symmetry codes: (ii) $-x + 1, -y, -z + 2$; (iii) $-x + 2, -y, -z + 1$; (iv) $-x, -y + 1, -z + 1$.

Table 10S. Geometrical parameters of the C−H···π contacts in the crystal of **SDB24C8⁻K⁺**.

D–H	***Cg*J**	**d(H···*Cg*J) [Å]**	**d(D··· *Cg*J) [Å]**	**<(C–H···*Cg*J) [°]**
C5–H5B	1^v	2.93	3.791(2)	148

*Cg*1 denotes the geometric centre of gravity of the aromatic ring delineated by the C1/C16/C20–C17 atoms (Fig. 1S). Symmetry code: (v) $-x + 1, -y + 1, -z + 1$.

Table 11S. Geometrical parameters of hydrogen bonds in the crystal of **SDB24C8⁻H_3O^+**.

D–H···A	**D–H [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(D–H···A) [°]**
O1W–H1W···O1	0.93(5)	2.51(5)	2.973(2)	111(4)
O1W–H1W···O8	0.93(5)	2.13(5)	3.031(2)	162(4)
O1W–H1WA···O2A	0.94(2)	2.15(2)	2.844(3)	130(2)
O1W–H1WA···O3A	0.94(2)	2.10(3)	2.952(6)	150(2)
O1W–H1WA···O2B	0.94(2)	2.21(2)	3.043(4)	147.4(19)
O1W–H1WA···O3B	0.94(2)	2.37(3)	3.117(6)	136.2(19)
O1W–H1WB···O9^i	0.95(2)	2.58(2)	2.996(2)	106.7(15)
O1W–H1WB···O1O^i	0.95(2)	1.95(2)	2.884(2)	169(2)
O1W–H1WC···O6	0.91(2)	2.04(2)	2.928(2)	164(4)
O1W–H1WC···O7A	0.91(2)	2.42(5)	2.895(3)	112(4)
C11–H11A···O9^{ii}	0.97	2.53	3.439(2)	156
C12–H12B···O11^{ii}	0.97	2.56	3.318(2)	135
C7A–H7AA···O11^{iii}	0.97	2.40	3.084(6)	127

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, y - 1, z + 1$; (iii) $-x + 2, -y + 1, -z + 1$.

Table 12S. Geometrical parameters of the C−H···π contacts in the crystal of **SDB24C8⁻H_3O^+**.

D–H	***Cg*J**	**d(H···*Cg*J) [Å]**	**d(D··· *Cg*J) [Å]**	**<(C–H···*Cg*J) [°]**
C2B–H2BA	2^{iv}	2.93	3.766(9)	145
C5B–H5BB	1^{iii}	2.62	3.555(6)	162

*Cg*1 and *Cg*2 denote the geometric centres of gravity of the aromatic rings delineated by the C1/C16/C20–C17 and C8–C9/C21–C24 atoms, respectively (Fig. 2S). Symmetry codes: (iii) $-x + 2, -y + 1, -z + 1$; (iv) $-x + 1, -y + 1, -z + 1$.