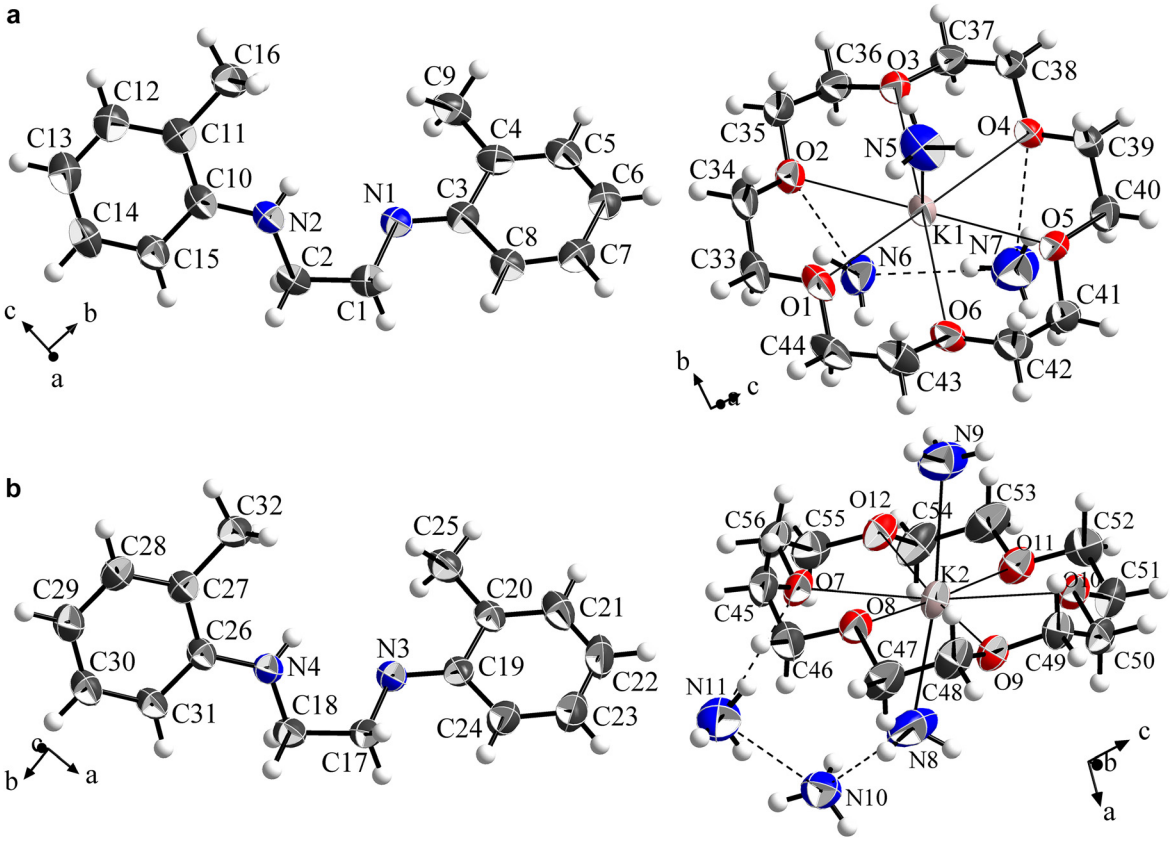
Christoph Wallach, Wilhelm Klein and Thomas F. Fässler*

Crystal structure of (1,4,7,10,13, 16-hexaoxacyclooctadecane-κ^6O_6) potassium(2-methylphenylamino)ethyl-2-methylphenylamide ammoniate (1/3.5), [K(18-crown-6)](*o*-$CH_3C_6H_4$)NH(CH_2)$_2$ N(*o*-$CH_3C_6H_4$) 3.5 NH_3, $C_{28}H_{53.5}KN_{5.5}O_6$



***Corresponding author: Thomas F. Fässler**, Technische Universität München, Fakultät für Chemie, Anorganische Chemie mit Schwerpunkt Neue Materialien, Lichtenbergstr. 4, 85747 Garching, Germany, E-mail: thomas.faessler@lrz.tum.de. https://orcid.org/0000-0001-9460-8882

Christoph Wallach and Wilhelm Klein, Technische Universität München, Fakultät für Chemie, Anorganische Chemie mit Schwerpunkt Neue Materialien, Lichtenbergstr. 4, 85747 Garching, Germany. https://orcid.org/0000-0002-9539-4852 (C. Wallach). https://orcid.org/0000-0002-6351-9921 (W. Klein)

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Abstract

$C_{28}H_{53.5}KN_{5.5}O_6$, monoclinic, *Pc* (no. 7), a = 18.7986(12) Å, b = 8.3431(6) Å, c = 22.4638(16) Å, β = 100.554(5)°, V = 3463.6(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0712, $wR_{ref}(F^2)$ = 0.2226, T = 150 K.

CCDC no.: 2180406

Table 1: Data collection and handling.

Crystal:	Yellow sphere
Size:	0.20 × 0.20 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.20 mm^{-1}
Diffractometer, scan mode:	STOE StadiVari, ω
θ_{max}, completeness:	26.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	40,821, 13,144, 0.075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 10,077
$N(param)_{refined}$:	745
Programs:	X-Area [1], SHELX [2, 3], Diamond [4]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained as an unintended side product from a synthesis aiming at functionalized Zintl cluster compounds [5]. All reactions were performed under the exclusion of oxygen and moisture using standard Schlenk line and glove box techniques. Glyoxal (Merck), BBr_3 (Sigma Aldrich) and 2-methylanilin (Sigma Aldrich) were used without further purification. 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6; Merck) was purified by sublimation. Bromo-1,3,2-diazaborolidine (DAB^{o-tol}–Br) was prepared according to a published procedure [5, 6]. K_4Ge_9 was prepared by fusing stoichiometric amounts of the elements in stainless-steel tubes at 650 °C. Liquid ammonia was dried over sodium metal for 2 h prior to condensing it onto the reaction mixture. K_4Ge_9 (80 mg, 98.7 µmol, 1 equiv.), DAB^{o-tol}–Br (32.5 mg, 98.7 µmol, 1 equiv.), and 18-crown-6 (47.0 mg, 177.7 µmol, 1.8 equiv.) were weighed into a Schlenk tube and liquid ammonia (2 mL) was condensed onto the reactants, causing the formation of a red solution. Yellow spherical crystals of the title compound were isolated from the reaction mixture after 9 months. An exact yield could not be determined due to the experimental setup.

Experimental details

A single crystal was selected under a microscope equipped with a light source using a cooling table [7]. Subsequently, the crystal was transferred under liquid nitrogen to the

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0781 (4)	0.6477 (9)	0.1624 (3)	0.0474 (16)
H1A	0.1301	0.6748	0.1668	0.057*
H1B	0.0609	0.6101	0.1205	0.057*
C2	0.0683 (4)	0.5156 (8)	0.2066 (3)	0.0459 (15)
H2A	0.0171	0.4807	0.1995	0.055*
H2B	0.0986	0.4222	0.2005	0.055*
C3	0.0432 (3)	0.9153 (8)	0.1380 (3)	0.0401 (14)
C4	0.0050 (4)	1.0635 (9)	0.1467 (3)	0.0472 (16)
C5	0.0092 (4)	1.1952 (9)	0.1102 (3)	0.0480 (16)
H5	−0.0162	1.2898	0.1170	0.058*
C6	0.0492 (4)	1.1947 (9)	0.0638 (3)	0.0520 (17)
H6	0.0504	1.2866	0.0390	0.062*
C7	0.0872 (4)	1.0581 (10)	0.0546 (3)	0.0501 (17)
H7	0.1157	1.0571	0.0238	0.060*
C8	0.0843 (3)	0.9210 (8)	0.0900 (3)	0.0444 (15)
H8	0.1105	0.8285	0.0821	0.053*
C9	−0.0393 (5)	1.0667 (10)	0.1955 (4)	0.059 (2)
H9A	−0.0544	1.1770	0.2016	0.089*
H9B	−0.0104	1.0259	0.2333	0.089*
H9C	−0.0823	0.9992	0.1837	0.089*
C10	0.0796 (4)	0.4788 (8)	0.3179 (3)	0.0448 (15)
C11	0.0742 (3)	0.5489 (9)	0.3738 (3)	0.0461 (15)
C12	0.0652 (4)	0.4477 (10)	0.4214 (4)	0.0545 (18)
H12	0.0612	0.4939	0.4593	0.065*
C13	0.0620 (4)	0.2828 (10)	0.4155 (4)	0.0588 (19)
H13	0.0550	0.2175	0.4486	0.071*
C14	0.0691 (4)	0.2147 (9)	0.3614 (4)	0.0560 (19)
H14	0.0686	0.1013	0.3574	0.067*
C15	0.0769 (4)	0.3102 (9)	0.3124 (4)	0.0497 (16)
H15	0.0805	0.2617	0.2748	0.060*
C16	0.0758 (5)	0.7287 (9)	0.3804 (4)	0.0569 (19)
H16A	0.1226	0.7695	0.3738	0.085*
H16B	0.0689	0.7576	0.4212	0.085*
H16C	0.0370	0.7758	0.3504	0.085*
C17	0.5542 (4)	0.2993 (8)	0.0840 (3)	0.0426 (14)
H17A	0.5564	0.2878	0.0405	0.051*
H17B	0.6007	0.3453	0.1049	0.051*
C18	0.4921 (4)	0.4121 (8)	0.0912 (3)	0.0458 (15)
H18A	0.4927	0.4336	0.1347	0.055*
H18B	0.4972	0.5154	0.0707	0.055*
C19	0.5945 (3)	0.0323 (8)	0.1040 (3)	0.0423 (14)
C20	0.5888 (4)	−0.1279 (8)	0.1273 (3)	0.0426 (14)
C21	0.6411 (5)	−0.2421 (10)	0.1236 (4)	0.0558 (18)
H21	0.6354	−0.3466	0.1387	0.067*
C22	0.7006 (5)	−0.2100 (11)	0.0989 (5)	0.068 (2)
H22	0.7359	−0.2906	0.0973	0.081*
C23	0.7090 (4)	−0.0556 (12)	0.0758 (5)	0.068 (2)
H23	0.7509	−0.0311	0.0595	0.082*
C24	0.6566 (4)	0.0612 (10)	0.0765 (4)	0.0539 (18)
H24	0.6620	0.1625	0.0585	0.065*
C25	0.5251 (4)	−0.1642 (9)	0.1570 (4)	0.0557 (18)
H25A	0.4801	−0.1441	0.1283	0.084*
H25B	0.5269	−0.0954	0.1926	0.084*
H25C	0.5268	−0.2769	0.1696	0.084*
C26	0.3578 (4)	0.4100 (8)	0.0596 (3)	0.0410 (14)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C27	0.2938 (4)	0.3161 (8)	0.0449 (3)	0.0425 (14)
C28	0.2276 (4)	0.3958 (10)	0.0356 (3)	0.0515 (17)
H28	0.1845	0.3347	0.0246	0.062*
C29	0.2218 (4)	0.5615 (9)	0.0416 (4)	0.0539 (18)
H29	0.1757	0.6118	0.0346	0.065*
C30	0.2843 (4)	0.6516 (9)	0.0581 (4)	0.0525 (17)
H30	0.2811	0.7644	0.0629	0.063*
C31	0.3521 (4)	0.5769 (8)	0.0674 (3)	0.0450 (15)
H31	0.3947	0.6392	0.0792	0.054*
C32	0.2985 (4)	0.1345 (9)	0.0411 (3)	0.0501 (16)
H32A	0.3217	0.1050	0.0070	0.075*
H32B	0.2497	0.0887	0.0351	0.075*
H32C	0.3271	0.0928	0.0788	0.075*
C33	0.2344 (4)	0.2584 (12)	0.1868 (4)	0.060 (2)
H33A	0.1838	0.2565	0.1646	0.072*
H33B	0.2657	0.2120	0.1602	0.072*
C34	0.2570 (4)	0.4279 (11)	0.2027 (4)	0.059 (2)
H34A	0.2480	0.4954	0.1658	0.071*
H34B	0.2283	0.4716	0.2317	0.071*
C35	0.3594 (5)	0.5892 (10)	0.2397 (4)	0.060 (2)
H35A	0.3288	0.6499	0.2633	0.072*
H35B	0.3582	0.6453	0.2006	0.072*
C36	0.4361 (5)	0.5814 (9)	0.2742 (4)	0.0563 (18)
H36A	0.4660	0.5151	0.2518	0.068*
H36B	0.4572	0.6904	0.2789	0.068*
C37	0.5049 (4)	0.5150 (9)	0.3708 (4)	0.0546 (18)
H37A	0.5220	0.6268	0.3775	0.065*
H37B	0.5402	0.4553	0.3516	0.065*
C38	0.4989 (4)	0.4388 (9)	0.4301 (4)	0.0508 (17)
H38A	0.5441	0.4557	0.4598	0.061*
H38B	0.4584	0.4873	0.4464	0.061*
C39	0.4814 (4)	0.1898 (9)	0.4748 (3)	0.0510 (17)
H39A	0.4416	0.2362	0.4926	0.061*
H39B	0.5271	0.2031	0.5043	0.061*
C40	0.4673 (4)	0.0143 (10)	0.4618 (4)	0.0546 (18)
H40A	0.5047	−0.0300	0.4405	0.065*
H40B	0.4693	−0.0453	0.5002	0.065*
C41	0.3819 (5)	−0.1664 (9)	0.4057 (4)	0.0571 (19)
H41A	0.3897	−0.2383	0.4413	0.069*
H41B	0.4146	−0.2002	0.3781	0.069*
C42	0.3044 (5)	−0.1756 (10)	0.3736 (4)	0.061 (2)
H42A	0.2906	−0.2888	0.3650	0.073*
H42B	0.2723	−0.1303	0.3997	0.073*
C43	0.2227 (4)	−0.0832 (12)	0.2878 (4)	0.063 (2)
H43A	0.1928	−0.0269	0.3132	0.076*
H43B	0.2041	−0.1938	0.2806	0.076*
C44	0.2183 (4)	0.0027 (12)	0.2285 (4)	0.067 (2)
H44A	0.2504	−0.0499	0.2040	0.080*
H44B	0.1681	−0.0009	0.2055	0.080*
C45	0.7084 (5)	0.0657 (11)	0.2523 (4)	0.061 (2)
H45A	0.6899	0.0554	0.2083	0.073*
H45B	0.6746	0.0095	0.2742	0.073*
C46	0.7824 (5)	−0.0085 (11)	0.2680 (4)	0.062 (2)
H46A	0.7814	−0.1194	0.2521	0.074*
H46B	0.8176	0.0543	0.2498	0.074*
C47	0.8760 (5)	−0.0672 (12)	0.3506 (5)	0.070 (2)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H47A	0.9105	0.0055	0.3357	0.084*
H47B	0.8809	−0.1755	0.3338	0.084*
C48	0.8910 (5)	−0.0722 (10)	0.4192 (4)	0.064 (2)
H48A	0.8533	−0.1362	0.4337	0.077*
H48B	0.9385	−0.1231	0.4339	0.077*
C49	0.9022 (4)	0.0896 (10)	0.5060 (3)	0.0551 (19)
H49A	0.9449	0.0235	0.5228	0.066*
H49B	0.8594	0.0441	0.5199	0.066*
C50	0.9141 (4)	0.2597 (12)	0.5280 (4)	0.060 (2)
H50A	0.9260	0.2618	0.5728	0.072*
H50B	0.9550	0.3078	0.5120	0.072*
C51	0.8576 (4)	0.5139 (10)	0.5244 (4)	0.0577 (19)
H51A	0.8951	0.5638	0.5047	0.069*
H51B	0.8732	0.5220	0.5688	0.069*
C52	0.7858 (5)	0.5990 (10)	0.5049 (4)	0.062 (2)
H52A	0.7473	0.5434	0.5215	0.075*
H52B	0.7892	0.7108	0.5199	0.075*
C53	0.7044 (5)	0.6816 (11)	0.4166 (5)	0.072 (3)
H53A	0.7094	0.7955	0.4291	0.087*
H53B	0.6636	0.6345	0.4328	0.087*
C54	0.6902 (5)	0.6696 (10)	0.3485 (5)	0.069 (2)
H54A	0.6489	0.7390	0.3311	0.083*
H54B	0.7333	0.7055	0.3326	0.083*
C55	0.6578 (5)	0.4885 (12)	0.2670 (4)	0.066 (2)
H55A	0.6986	0.5284	0.2489	0.080*
H55B	0.6141	0.5514	0.2501	0.080*
C56	0.6450 (4)	0.3131 (12)	0.2523 (4)	0.062 (2)
H56A	0.6091	0.2690	0.2752	0.075*
H56B	0.6259	0.2993	0.2085	0.075*
K1	0.36436 (7)	0.21464 (19)	0.32711 (7)	0.0464 (4)
K2	0.78875 (8)	0.29735 (19)	0.38429 (7)	0.0499 (4)
N1	0.0376 (3)	0.7889 (7)	0.1739 (3)	0.0422 (12)
N2	0.0892 (3)	0.5747 (8)	0.2686 (3)	0.0451 (13)
H2	0.071 (4)	0.661 (11)	0.272 (4)	0.05 (2)*
N3	0.5433 (3)	0.1426 (7)	0.1096 (3)	0.0416 (12)
N4	0.4243 (3)	0.3337 (7)	0.0639 (3)	0.0435 (13)
H4	0.426 (5)	0.235 (12)	0.075 (4)	0.07 (3)*
N5	0.2640 (4)	0.3465 (12)	0.3948 (4)	0.080 (2)
H5A	0.2710	0.4542	0.3986	0.121*
H5B	0.2709	0.3007	0.4321	0.121*
H5C	0.2181	0.3267	0.3751	0.121*
N6	0.4340 (4)	0.1480 (9)	0.2097 (3)	0.0641 (18)
H6A	0.4018	0.2277	0.1967	0.096*
H6B	0.4112	0.0516	0.2042	0.096*
H6C	0.4706	0.1508	0.1882	0.096*
N7	0.5315 (6)	−0.0043 (12)	0.3261 (5)	0.098 (3)
H7A	0.5092	0.0464	0.2918	0.148*
H7B	0.5217	0.0484	0.3591	0.148*
H7C	0.5150	−0.1068	0.3261	0.148*
N8	0.8899 (4)	0.4399 (14)	0.3199 (5)	0.101 (3)
H8A	0.8675	0.5182	0.2951	0.151*
H8B	0.9074	0.3638	0.2973	0.151*
H8C	0.9271	0.4833	0.3467	0.151*
N9	0.6663 (4)	0.1920 (12)	0.4337 (4)	0.088 (3)
H9D	0.6513	0.0948	0.4178	0.131*
H9E	0.6297	0.2643	0.4244	0.131*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H9F	0.6790	0.1836	0.4747	0.131*
N10	0.8830 (4)	0.6654 (9)	0.2025 (4)	0.0683 (19)
H10A	0.8554	0.7468	0.2128	0.102*
H10B	0.8740	0.6531	0.1615	0.102*
H10C	0.9307	0.6889	0.2152	0.102*
N11	0.7914 (5)	0.3377 (13)	0.1559 (4)	0.094 (3)
H11A	0.8277	0.4113	0.1630	0.141*
H11B	0.8084	0.2452	0.1423	0.141*
H11C	0.7750	0.3181	0.1909	0.141*
O1	0.2405 (3)	0.1667 (7)	0.2405 (2)	0.0561 (13)
O2	0.3322 (3)	0.4312 (6)	0.2289 (2)	0.0510 (12)
O3	0.4354 (2)	0.5128 (6)	0.3322 (2)	0.0459 (11)
O4	0.4864 (2)	0.2712 (6)	0.4198 (2)	0.0447 (11)
O5	0.3968 (3)	−0.0033 (6)	0.4245 (2)	0.0469 (11)
O6	0.2963 (3)	−0.0873 (6)	0.3183 (2)	0.0516 (12)
O7	0.7129 (3)	0.2303 (7)	0.2689 (2)	0.0539 (12)
O8	0.8028 (3)	−0.0090 (7)	0.3326 (2)	0.0550 (12)
O9	0.8910 (3)	0.0873 (6)	0.4417 (2)	0.0494 (11)
O10	0.8481 (3)	0.3504 (6)	0.5069 (2)	0.0507 (12)
O11	0.7696 (3)	0.5970 (6)	0.4397 (3)	0.0574 (13)
O12	0.6743 (3)	0.5073 (6)	0.3320 (2)	0.0544 (12)

diffractometer (STOE StadiVari) equipped with a PILATUS 300 K detector (DECTRIS) and a Mo Kα radiation source (λ = 0.71073 Å). For the data collection the crystal was cooled in a 150 K cold stream of dry nitrogen. The single crystal structure was determined by direct methods using the program SHELXS-97 [2]. Structure refinements were performed by full-matrix least-squares calculations against F^2 (SHELXL-2014) [3]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms at N2 and N4 were located from the difference Fourier map and were refined with independent positional and isotropic displacement parameters. No similar strong residual electron densities could be detected at N1 and N3. Some hydrogen atoms of the ammonia molecules around N6, N7, N10, and N11 were localized from the difference Fourier map, the remaining ones were positioned in direction to close neighboured atoms where hydrogen bonds are probable. The methyl and ammonia H atoms were finally refined using a riding model with U_{iso} set to 1.5 U_{eq}(C) and U_{eq}(N), respectively, all other H atoms with U_{iso} set to 1.2 U_{eq}(C) [3].

Comment

The title compound (**1**) consists of an ion pair of the cationic coordination complex $[K(18\text{-crown-6})]^+$ and the $[(o\text{-}CH_3C_6H_4)NH(CH_2)_2N(o\text{-}CH_3C_6H_4)]^-$ anion, and crystallizes including 3.5 molecules of ammonia per formula unit. **1** crystallizes in the monoclinic space group *Pc* with four formula units per unit cell, the asymmetric unit is formed by two formula units. The anion is the amide of N1,N2-di(o-$CH_3C_6H_4$)ethylene-1,2-diamine, which serves a reactant in the synthesis of the bromo-1,3,2-diazaborolidine $DAB^{o\text{–}tol}$–Br [6]. Most probably, trace amounts of N1,N2-di(o-$CH_3C_6H_4$)ethylene-1,2-diamine remained in the synthesized precursor $DAB^{o\text{–}tol}$–Br, which were transferred into the reaction mixture in liquid ammonia by weighing in the precursor. Even though an exact formation mechanism for the generation of the amide cannot be determined, the generation of amides in liquid ammonia or ethylenediamine is an oftentimes described process [8–11].

The two crystallographically independent anions (**1a**, **1b**) are quite similarly shaped. The interatomic distances of the central ethanediamine groups [C1–C2 1.517(11) Å, C17–C18 1.531(10) Å, C1–N1 1.451(9) Å, C17–N3 1.458(8) Å, C2–N2 1.462(10) Å, C18–N4 1.464(9) Å] clearly indicate single bonds. Also, the torsion angles of the two amine substituents around the C1–C2 and C17–C18 bonds of 55.6° and 54.9°, respectively, are in the expected range for this. In contrast, the N–C bonds to the aryl groups of 1.343(9) Å (N1–C3), 1.403(9) Å (N2–C10), 1.354(9) Å (N3–C19), and 1.390(9) Å (N4–C26) are significantly shorter, also shorter than those in related compounds such as *o*-methylaniline (N–C 1.447 Å) [12], suggesting a partial double bond character, which is even slightly stronger expressed for the negatively charged N atom. This is supported by the torsion angles of the substituents of the N–C(aryl) bond, which are nearly planar around the amide N atom at 179.3° (**1a**) and 179.4° (**1b**), and deviate only slightly from planarity even with a protonated N atom [156.9° (**1a**) and 166.5° (**1a**)]. The relative inclination of the planes of the aromatic rings is 33.7° (**1a**) and 41.3° (**1b**).

The potassium cations are coordinated in equatorial positions by oxygen atoms of [18]crown-6 molecules and are located in the molecular plane. The mean interatomic distances K–O, C–O, and C–C were determined to 2.814, 1.431, and 1.507 Å, respectively. Additionally, ammonia molecules coordinate the potassium cations in axial positions. For K2, two NH_3 molecules are observed at distances of 2.852(9) Å (N8) and 2.871(9) Å (N9), forming an almost linear H_3N–K–NH_3 unit with an angle of 168.6(3)°. K1 is coordinated by an NH_3 molecule at 2.851(8) Å, while on the opposite side of the molecule there are NH_3 molecules at a greater distance from the K^+ ion, which form hydrogen bonds to oxygen atoms of the crown ether molecule [13]. The longish anions are arranged with their major extension roughly along the crystallographic *c* (**1a**) or *a* (**1b**) axes and stacked in the *b* direction, respectively. The cation

complexes and the solvent molecules are located in the channels parallel to *b* formed in this way.

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