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Crystal structure of (1,4,7,10,13,16-hexaoxacyclooctadecane- $\kappa^6 O_6$) 1,2,3,4,5-pentamethyl-cyclopenta-2,4-dien-1-yl(potassium, rubidium) – ammonia (1/2), $[K_{0.3}Rb_{0.7}(18\text{-crown-6})]Cp^* \cdot 2 NH_3$, $C_{22}H_{45}K_{0.3}N_2O_6Rb_{0.7}$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.10 × 0.10 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.43 mm ⁻¹
Diffraction, scan mode:	Oxford Xcalibur 3, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	57130, 5339, 0.186
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1974
$N(\text{param})_{\text{refined}}$:	286
Programs:	CrysAlis ^{CCD} , CrysAlis ^{RED} [1], SHELX [2, 3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb ^a	0.50715(4)	0.35028(2)	0.13261(2)	0.02597(13)
K ^b	0.50715(4)	0.35028(2)	0.13261(2)	0.02597(13)
O1	0.3786(2)	0.30253(16)	0.05396(8)	0.0358(8)
O2	0.6508(2)	0.33550(16)	0.04816(8)	0.0374(8)
O3	0.7956(2)	0.35636(18)	0.11999(8)	0.0408(7)
O4	0.6969(3)	0.27707(17)	0.19030(8)	0.0411(7)
O5	0.4287(3)	0.23053(16)	0.20054(8)	0.0410(7)
O6	0.3021(2)	0.21759(15)	0.12454(8)	0.0375(7)
C1	0.4478(3)	0.3058(3)	0.01615(12)	0.0412(12)
H1A	0.3872	0.3223	−0.0060	0.049*
H1B	0.4842	0.2510	0.0095	0.049*
C2	0.5561(4)	0.3665(3)	0.02002(12)	0.0452(13)
H2A	0.5979	0.3757	−0.0068	0.054*
H2B	0.5208	0.4196	0.0299	0.054*
C3	0.7649(4)	0.3879(3)	0.05042(12)	0.0461(12)
H3A	0.7384	0.4440	0.0586	0.055*
H3B	0.8083	0.3910	0.0235	0.055*
C4	0.8573(3)	0.3527(3)	0.08102(12)	0.0472(11)
H4A	0.8782	0.2951	0.0740	0.057*
H4B	0.9403	0.3845	0.0813	0.057*
C5	0.8760(4)	0.3237(3)	0.15085(14)	0.0579(15)
H5A	0.9603	0.3542	0.1518	0.070*
H5B	0.8959	0.2655	0.1448	0.070*
C6	0.8094(4)	0.3296(3)	0.19079(13)	0.0567(14)
H6A	0.8704	0.3127	0.2127	0.068*
H6B	0.7820	0.3870	0.1959	0.068*
C7	0.6339(4)	0.2698(3)	0.22888(12)	0.0527(13)
H7A	0.5915	0.3225	0.2363	0.063*
H7B	0.6995	0.2559	0.2501	0.063*

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Abstract

$C_{22}H_{45}K_{0.26}N_2O_6Rb_{0.74}$, orthorhombic, $Pbca$ (no. 61), $a = 10.1587(8)$ Å, $b = 16.2842(15)$ Å, $c = 32.862(3)$ Å, $V = 5436.2(8)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0386$, $wR_{\text{ref}}(F^2) = 0.0616$, $T = 120(2)$ K.

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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.

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Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C8	0.5333(4)	0.2038(3)	0.22595(13)	0.0593(15)
H8A	0.5735	0.1535	0.2145	0.071*
H8B	0.4990	0.1907	0.2534	0.071*
C9	0.3424(4)	0.1645(2)	0.19021(12)	0.0462(12)
H9A	0.3002	0.1426	0.2151	0.055*
H9B	0.3929	0.1196	0.1772	0.055*
C10	0.2396(4)	0.1957(2)	0.16153(12)	0.0424(12)
H10A	0.1729	0.1525	0.1565	0.051*
H10B	0.1948	0.2441	0.1734	0.051*
C11	0.2105(3)	0.2392(3)	0.09376(12)	0.0411(12)
H11A	0.1724	0.2938	0.0997	0.049*
H11B	0.1380	0.1986	0.0931	0.049*
C12	0.2792(3)	0.2409(2)	0.05357(11)	0.0390(11)
H12A	0.3195	0.1866	0.0481	0.047*
H12B	0.2149	0.2526	0.0317	0.047*
C13	0.3576(4)	0.5134(2)	0.11868(12)	0.0304(10)
C14	0.4870(4)	0.54372(19)	0.12157(9)	0.0263(9)
C15	0.5269(4)	0.5370(2)	0.16226(11)	0.0296(10)
C16	0.4243(4)	0.5028(2)	0.18490(12)	0.0309(10)
C17	0.3190(4)	0.4878(2)	0.15735(14)	0.0350(11)
C18	0.2731(3)	0.5089(2)	0.08080(12)	0.0432(12)
H18A	0.1984	0.5465	0.0835	0.065*
H18B	0.2405	0.4527	0.0773	0.065*
H18C	0.3258	0.5244	0.0570	0.065*
C19	0.5689(3)	0.5799(2)	0.08734(11)	0.0359(11)
H19A	0.5600	0.6398	0.0874	0.054*
H19B	0.5380	0.5581	0.0612	0.054*
H19C	0.6615	0.5651	0.0913	0.054*
C20	0.6598(3)	0.5642(2)	0.17835(12)	0.0434(12)
H20A	0.6709	0.6232	0.1736	0.065*
H20B	0.7297	0.5340	0.1642	0.065*
H20C	0.6648	0.5529	0.2076	0.065*
C21	0.4240(4)	0.4842(2)	0.22995(12)	0.0547(13)
H21A	0.3516	0.5139	0.2430	0.082*
H21B	0.5078	0.5017	0.2419	0.082*
H21C	0.4125	0.4251	0.2341	0.082*
C22	0.1884(3)	0.4493(2)	0.16857(13)	0.0554(13)
H22A	0.1646	0.4652	0.1964	0.083*
H22B	0.1958	0.3893	0.1670	0.083*
H22C	0.1204	0.4682	0.1496	0.083*
N1	0.5910(3)	0.1550(2)	0.09342(10)	0.0795(12)
H1C	0.6373	0.1201	0.1096	0.119*
H1D	0.5069	0.1590	0.1027	0.119*
H1E	0.6295	0.2055	0.0939	0.119*
N2	0.5881(3)	0.0832(2)	0.00252(10)	0.0745(13)
H2C	0.6560	0.0467	0.0028	0.112*
H2D	0.5713	0.1003	0.0284	0.112*
H2E	0.6101	0.1271	−0.0132	0.112*

^aOccupancy: 0.737(3), ^bOccupancy: 0.263(3).

Source of material

The Zintl phase K₆Rb₆Si₁₇ [5] was prepared from a stoichiometric mixture of the elements in a sealed tantalum container, which was enclosed in an evacuated fused silica tube. The mixture was heated to 800 °C for 15 h and slowly

cooled to room temperature with a rate of 0.5 °C/min. Zn₂(Cp*)₂ was prepared as described in literature [6]. 92 mg K₆Rb₆Si₁₇, 36 mg 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6; Merck, p. a.), and 25 mg Zn₂(Cp*)₂ were given into a dry Schlenk vessel and ca. 2 mL NH₃ (Westfalen, 99.999%, stored over elemental Na) were condensed on this. The orange-red solution was stored at −70 °C for 19 weeks, after this time yellow crystals of the title compound were found. An appropriate crystal was selected under perfluoroalkylether in a stream of cold nitrogen gas.

Experimental details

The alkali metal atom with mixed K/Rb occupation has been refined with the same positional and anisotropic displacement parameters and site occupation factors which sum up to 100%. No clue for a positional split of the elements was observed. The methylene and methyl H atoms have been refined using a riding model with U_{iso} set to 1.2 and 1.5 $U_{\text{eq}}(\text{C})$, respectively. The H atoms bound to N Atoms have been located from the difference Fourier map and refined with a riding model and an U_{iso} of 1.5 $U_{\text{eq}}(\text{N})$ [3].

Comment

Liquid ammonia has been found to be a highly suitable solvent for Si-containing Zintl cluster compounds [7, 8]. In the course of our investigations of the behaviour and reactivity of such compounds in comparison to the known Ge compounds [9, 10], K₆Rb₆Si₁₇ was dissolved in liquid ammonia in presence of 18-crown-6 and the metalorganic reagent Zn₂(Cp*)₂. After several weeks at −70 °C yellow crystals of the title compound have been found besides orange crystals of K_{0.8}Rb_{3.2}Si₉ × 5 NH₃ [7]. It has to be noted that in both compounds which have been obtained as solid precipitates from these solutions, a considerable excess of Rb was found although equimolar amounts of K and Rb were applied. The remaining K as well as other parts of the reaction mixture, Zn and Si₄ clusters, were not found in a solid product of this experiment.

[K_{0.3}Rb_{0.7}(18-crown-6)]Cp* × 2 NH₃ crystallizes in space group *Pbca* with one formula unit as asymmetric unit and all atoms at general positions. At the cation site, a mixed occupation of 73.7(3)% Rb and 26.3(3)% K was found which corresponds with the mixed composition of the applied precursor. The cation is coordinated by one 18-crown-6 ligand and one Cp* anion. According to the main elemental site occupation by Rb and its preferred coordination environment by 18-crown-6 in a “sunrise” conformation [11], the cation is situated near the centre of the 18-crown-6 molecule but apart from its ring plane shifted in direction of the Cp* anion. The presence of the crown ether causes the formation of molecular units differing from pure RbCp* which forms polymeric

“multidecker” strands [12], but similar to the effect of diaza-18-crown-6 on $RbCp^*$ [13]. Rb is bound to the Cp^* ligand *via* five short Rb—C bonds between 3.055(4) Å and 3.199(3) Å very similar to those observed for the η^5 coordinations in $[Rb(18\text{-crown-6})]Cp^*$ [12] and $[Rb(18\text{-crown-6})]Cp^* \times thf$ [14]. All C atoms of the Cp^* ligand are in plane and the cyclopentadienyl ring is an almost regular pentagon (C—C bond lengths between 1.394(5) Å and 1.423(5) Å, C—C—C angles between 106.9(3)° and 108.9(3)°, clearly different from the shape of the neutral Cp^*-H molecule [15], suggesting that the negative charge is located at Cp^* . Confirming this and additionally excluding the presence of possible amide anions instead, for each of the ammonia molecules three H atoms could have been located from the Fourier map. Some of these H atoms are situated close to the shortest N—O and N—N atom connections indicating the formation of hydrogen bonds. The presence of N—H $\cdots$ O hydrogen bonds resemble to the conditions in the cation-free adduct of 18-crown-6 and ammonia showing similar shortest N—O distances [16].

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