Christina Fischer, Wilhelm Klein and Thomas F. Fässler*

Crystal structure of (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane- $\kappa^8 N_2$, O_6) potassium cyclopentadienide, $[K([2.2.2]crypt)]Cp$, $C_{23}H_{41}KN_2O_6$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.20 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.25 mm ⁻¹
Diffractometer, scan mode:	Oxford Xcalibur 3, φ and π
$\theta_{\max}$, completeness:	28.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	32,316, 6125, 0.047
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4029
$N(\text{param})_{\text{refined}}$:	453
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

CCDC no.: 2103410

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 Zintl phase K_4Sn_9 was prepared from stoichiometric mixtures of the elements in steel containers, which were encapsulated in an evacuated fused silica tube. The mixture was heated to 550 °C for 46 h and slowly cooled to room temperature with a rate of 1 °C/min. Biscyclopentadienyl-germanium ($GeCp_2$) was prepared as described in literature [5–7]. 91.9 mg K_4Sn_9 (0.075 mmol), 15.2 mg 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ([2.2.2]cryptand; 0.3 mmol; Merck, p. a.), and 15.2 mg $GeCp_2$ (0.075 mmol) were given into a dry Schlenk vessel and ca. 2 ml NH_3 (Westfalen, 99.999%, stored over elemental Na) were condensed on this. The red solution was stored at –70 °C for 11 months, after this time colourless crystals of the title compound were obtained. A crystal appropriate for X-ray diffraction measurements was selected under perfluoroalkylether in a stream of cold nitrogen gas.

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Abstract

$C_{23}H_{41}KN_2O_6$, monoclinic, $P2_1/c$ (no. 14), $a = 10.9817(6)$ Å, $b = 23.8330(15)$ Å, $c = 9.7379(7)$ Å, $\beta = 94.705(5)^\circ$, $V = 2540.1(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0327$, $wR_{\text{ref}}(F^2) = 0.0682$, $T = 120$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K	0.37019 (3)	0.13897 (2)	0.60803 (3)	0.01955 (8)
N1	0.12350 (10)	0.11496 (4)	0.47325 (11)	0.0203 (2)
N2	0.62089 (10)	0.16191 (5)	0.74401 (11)	0.0203 (2)
O1	0.34765 (8)	0.08353 (4)	0.34195 (9)	0.0231 (2)
O2	0.57483 (8)	0.08797 (4)	0.50517 (9)	0.0224 (2)
O3	0.42672 (8)	0.10438 (4)	0.88158 (9)	0.0222 (2)
O4	0.20947 (8)	0.06480 (4)	0.73713 (9)	0.0227 (2)
O5	0.21257 (8)	0.22836 (4)	0.54725 (10)	0.0268 (2)
O6	0.45760 (8)	0.25150 (4)	0.63071 (9)	0.0239 (2)
C1	0.13196 (13)	0.10268 (6)	0.32584 (15)	0.0253 (3)
H1A	0.0514 (15)	0.0896 (6)	0.2814 (15)	0.035 (4)*
H1B	0.1518 (12)	0.1381 (6)	0.2783 (14)	0.024 (4)*
C2	0.22976 (13)	0.06073 (6)	0.30041 (16)	0.0257 (3)
H2A	0.2197 (12)	0.0250 (6)	0.3553 (13)	0.024 (4)*
H2B	0.2237 (12)	0.0533 (6)	0.1985 (15)	0.027 (4)*
C3	0.44048 (13)	0.04239 (6)	0.33627 (16)	0.0236 (3)
H3A	0.4284 (13)	0.0121 (6)	0.4015 (14)	0.032 (4)*
H3B	0.4361 (12)	0.0253 (5)	0.2427 (14)	0.020 (4)*
C4	0.56307 (13)	0.06878 (7)	0.36642 (15)	0.0255 (3)
H4A	0.6258 (13)	0.0398 (6)	0.3550 (14)	0.028 (4)*
H4B	0.5711 (13)	0.0991 (6)	0.3060 (15)	0.031 (4)*
C5	0.69057 (13)	0.11418 (7)	0.53806 (15)	0.0265 (3)
H5A	0.6958 (12)	0.1511 (6)	0.4873 (13)	0.023 (4)*
H5B	0.7539 (14)	0.0903 (6)	0.5092 (14)	0.033 (4)*
C6	0.70998 (13)	0.12309 (6)	0.69139 (15)	0.0253 (3)
H6A	0.7027 (12)	0.0879 (6)	0.7346 (13)	0.018 (3)*
H6B	0.7931 (13)	0.1362 (6)	0.7119 (14)	0.026 (4)*
C7	0.61742 (13)	0.15441 (6)	0.89417 (14)	0.0230 (3)
H7A	0.6971 (14)	0.1559 (6)	0.9402 (14)	0.031 (4)*
H7B	0.5708 (12)	0.1858 (5)	0.9326 (12)	0.016 (3)*
C8	0.55280 (12)	0.10190 (6)	0.93247 (15)	0.0232 (3)
H8A	0.5583 (12)	0.0970 (5)	1.0314 (15)	0.022 (4)*
H8B	0.5894 (13)	0.0667 (6)	0.8941 (14)	0.030 (4)*
C9	0.36129 (13)	0.05691 (6)	0.92401 (16)	0.0247 (3)
H9A	0.3746 (13)	0.0527 (6)	1.0248 (16)	0.029 (4)*
H9B	0.3914 (14)	0.0219 (6)	0.8835 (14)	0.033 (4)*
C10	0.22805 (13)	0.06385 (6)	0.88335 (14)	0.0232 (3)
H10A	0.1978 (12)	0.0985 (6)	0.9228 (13)	0.021 (4)*
H10B	0.1846 (12)	0.0320 (5)	0.9218 (13)	0.019 (3)*
C11	0.08261 (13)	0.06706 (7)	0.69296 (15)	0.0264 (3)
H11A	0.0423 (14)	0.0330 (6)	0.7285 (15)	0.036 (4)*
H11B	0.0457 (13)	0.1011 (6)	0.7342 (14)	0.028 (4)*
C12	0.06761 (13)	0.06713 (6)	0.53823 (15)	0.0247 (3)
H12A	−0.0221 (15)	0.0653 (6)	0.5095 (15)	0.036 (4)*
H12B	0.1020 (12)	0.0322 (6)	0.5092 (13)	0.019 (4)*
C13	0.04758 (13)	0.16510 (6)	0.48871 (16)	0.0250 (3)
H13A	0.0283 (12)	0.1672 (5)	0.5859 (15)	0.022 (4)*
H13B	−0.0294 (14)	0.1626 (6)	0.4304 (14)	0.030 (4)*
C14	0.10737 (13)	0.21931 (6)	0.45306 (17)	0.0271 (3)
H14A	0.0484 (12)	0.2497 (6)	0.4633 (13)	0.022 (4)*
H14B	0.1326 (13)	0.2213 (6)	0.3564 (15)	0.032 (4)*
C15	0.26416 (14)	0.28219 (6)	0.52912 (17)	0.0280 (3)
H15A	0.2030 (13)	0.3105 (6)	0.5380 (14)	0.030 (4)*
H15B	0.2964 (14)	0.2842 (6)	0.4360 (16)	0.035 (4)*
C16	0.36374 (13)	0.29203 (6)	0.64038 (16)	0.0268 (3)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
H16A	0.3984 (13)	0.3289 (6)	0.6307 (13)	0.031 (4)*
H16B	0.3312 (12)	0.2890 (5)	0.7334 (14)	0.021 (4)*
C17	0.55787 (13)	0.26237 (6)	0.72976 (16)	0.0275 (3)
H17A	0.5278 (12)	0.2630 (6)	0.8257 (14)	0.025 (4)*
H17B	0.5884 (13)	0.3009 (6)	0.7127 (14)	0.031 (4)*
C18	0.65696 (13)	0.21978 (6)	0.71538 (17)	0.0267 (3)
H18A	0.6809 (13)	0.2224 (6)	0.6222 (15)	0.028 (4)*
H18B	0.7269 (13)	0.2308 (6)	0.7787 (14)	0.025 (4)*
C19	0.82887 (12)	0.08625 (6)	0.14593 (15)	0.0248 (3)
H19	0.7900 (13)	0.0546 (6)	0.1859 (14)	0.025 (4)*
C20	0.90191 (12)	0.08470 (6)	0.03450 (15)	0.0241 (3)
H20	0.9220 (13)	0.0529 (6)	−0.0155 (14)	0.026 (4)*
C21	0.94360 (12)	0.13917 (6)	0.01261 (14)	0.0217 (3)
H21	0.9954 (13)	0.1499 (6)	−0.0544 (14)	0.025 (4)*
C22	0.89716 (12)	0.17456 (6)	0.11033 (14)	0.0230 (3)
H22	0.9106 (12)	0.2145 (6)	0.1172 (13)	0.021 (4)*
C23	0.82596 (12)	0.14175 (6)	0.19253 (14)	0.0226 (3)
H23	0.7849 (12)	0.1547 (5)	0.2659 (14)	0.020 (4)*

Experimental details

All H atoms have been located from the difference Fourier map and refined with free atomic coordinates and isotropic displacement parameters [3].

Comment

For the study of behaviour and reactivity of tetrel element Zintl compounds in solution, liquid ammonia has been found to be highly suitable [8, 9]. To support the dissolution of the solid Zintl compounds often sequestering agents like crown ethers or cryptands are necessary. During our investigations with the goal to extend or interconnect such clusters via additional tetrel or transition metal atoms [9, 10], [2.2.2]cryptand has been used to dissolve K_4Sn_9 in liquid ammonia in presence of GeCp_2 . As found in several examples where the Cp component forms well-crystallised side products [9, 11–13] the title compound has been obtained as a crystallised product of a partial metathesis reaction, while the remaining ingredients, Ge as well as $[\text{Sn}_9]^{4-}$ cluster anions, were not found as parts of crystalline phases after this experiment.

$[\text{K}(\text{crypt-222})]\text{Cp}$ crystallises in space group $P2_1/c$ with one formula unit as the asymmetric unit and all atoms are at general positions. The cyclopentadienyl counter anion is formed by a regular pentagon of C atoms with C–C distances in a very narrow range of 1.399(2) and 1.402(2) Å and C–C–C angles are between 107.67(12) and 108.29(12)°, all

atoms are perfectly planar (angle sum 540.00°). The H atoms of the anion, which are freely refined without any constraints, are in plane, too, and are found in C–H distances between 0.928(13) and 0.965(14) Å. The potassium cation is coordinated by one [2.2.2]cryptand molecule with K–O distances between 2.7781(9) and 2.9009(9) Å and K–N distances of 2.9675(11) and 3.0056(11) Å. Separated this way, no close contacts between K^+ and Cp are observed. The shortest intermolecular distances between the K atom and atoms belonging to the anion are K–H19 (5.38 Å) and K–C19 (6.34 Å). This is in contrast to pure KCp which is found to crystallise in polymeric “multidecker” strands [14, 15], while the presence of crown ether often induces the formation of molecular [(18-crown-6)K(Cp)] [16] or even double-sandwich-like [(18-crown-6)K(Cp)K(18-crown-6)]⁺ units [17], all including η^5 coordination of the K atoms with K–C distances around 3 Å. In the title compound the (K[2.2.2]crypt) complex and the Cp anion are packed in an 1:1 ion packing with identical ten-membered polyhedra of three equally charged ions and seven oppositely charged ions. The shortest C–C distances between different Cp[−] ions are 4.65 Å and possible π – π interactions are not observed. Hydrogen bonds to electronegative O or N atoms of the cryptand which are sometimes formed e.g. with crown ether molecules [13], can also be neglected as the shortest intermolecular C–O distance is 3.81 Å (H...O 2.94 Å, C–H...O 150°). Thus, in absence of any noteworthy interactions to neighbouring entities the anion in the title compound can be considered as an example of a “naked” cyclopentadienyl group.

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