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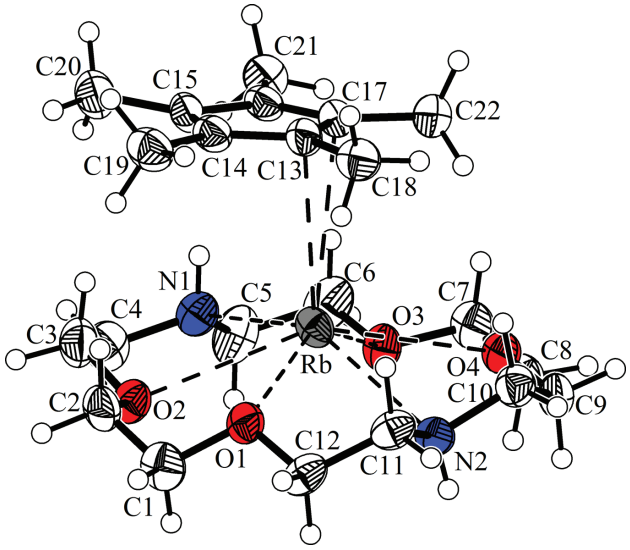
Crystal structure of [(1,2-η)-1,2,3,4,5-pentamethyl-cyclopenta-2,4-dien-1-yl] (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-κ^6N_2,O_4) rubidium (I), [Rb(diaza-18-crown-6)]Cp*, $C_{22}H_{41}N_2O_4Rb$



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Abstract

$C_{22}H_{41}N_2O_4Rb$, monoclinic, $P2_1/n$ (no. 14), $a = 10.8160(9)$ Å, $b = 17.7253(16)$ Å, $c = 13.2179(12)$ Å, $\beta = 93.961(8)°$, $V = 2528.0(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0376$, $wR_{ref}(F^2) = 0.0694$, $T = 120(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The Zintl phase $Rb_{12}Si_{17}$ [5] was prepared from stoichiometric mixtures of the elements in sealed tantalum containers, which were encapsulated 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. Bis(pentamethylcyclopentadienyl)zinc ($ZnCp^*_2$) was prepared as described in literature [6]. 113 mg $Rb_{12}Si_{17}$, 35 mg 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (diaza-18-crown-6; Merck, p. a.), and 25 mg $Zn_2Cp^*_2$ were placed in into a dry Schlenk vessel and *ca* 2 mL NH_3 (Westfalen, 99.999%, stored over elemental Na) were condensed on this. The obtained light yellow solution was stored at −70 °C for 11 months, 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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.15 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.99 mm^{-1}
Diffractometer, scan mode:	Oxford Xcalibur 3, ω and π
θ_{max}, completeness:	26.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	26792, 4963, 0.100
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2435
$N(param)_{refined}$:	272
Programs:	CrysAlis [1], SHELX [2, 3], Diamond [4]

Experimental details

The methylene and methyl H atoms have been refined using a riding model with U_{iso} set to 1.2 and 1.5 U_{eq}(C), respectively. The H atoms bound to N Atoms have been located from the difference Fourier map and refined with free atomic coordinates and an U_{iso} of 1.2 U_{eq}(N) [3].

Comment

During our investigations of the behaviour and reactivity of Si containing Zintl compounds in solution with the goal to synthesize transition metal complexes with Si clusters as ligands analogously to the known Ge compounds [7], liquid ammonia has been found to be a highly suitable solvent [8, 9]. For supporting the dissolution of the solid Zintl compounds often sequestering agents like crown ethers or cryptands are necessary. In the present experiment, diaza-18-crown-6 has been used to dissolve $Rb_{12}Si_{17}$ in liquid ammonia in presence

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Rb	0.44660(3)	0.33795(2)	0.34703(3)	0.03586(11)
O1	0.7034(2)	0.30542(13)	0.30666(16)	0.0386(6)
C1	0.7869(3)	0.3673(2)	0.3013(3)	0.0477(11)
H1A	0.8607	0.3515	0.2664	0.057*
H1B	0.8147	0.3841	0.3706	0.057*
C2	0.7224(3)	0.4307(2)	0.2443(3)	0.0465(11)
H2A	0.7828	0.4707	0.2304	0.056*
H2B	0.6847	0.4121	0.1786	0.056*
O2	0.6287(2)	0.46052(12)	0.30345(16)	0.0404(6)
C3	0.5591(4)	0.5184(2)	0.2503(3)	0.0531(12)
H3A	0.5114	0.4968	0.1906	0.064*
H3B	0.6159	0.5573	0.2262	0.064*
C4	0.4717(4)	0.5537(2)	0.3211(3)	0.0531(11)
H4A	0.5196	0.5727	0.3823	0.064*
H4B	0.4288	0.5971	0.2870	0.064*
N1	0.3790(3)	0.49846(17)	0.3511(2)	0.0430(9)
H1	0.329(3)	0.4852(19)	0.295(2)	0.052*
C5	0.3108(4)	0.5236(2)	0.4372(3)	0.0581(12)
H5A	0.2661	0.5709	0.4185	0.070*
H5B	0.3706	0.5347	0.4954	0.070*
C6	0.2197(4)	0.4658(2)	0.4685(3)	0.0576(12)
H6A	0.1724	0.4863	0.5239	0.069*
H6B	0.1603	0.4538	0.4105	0.069*
O3	0.2834(2)	0.39923(13)	0.50214(17)	0.0406(6)
C7	0.2026(3)	0.3442(2)	0.5399(2)	0.0475(10)
H7A	0.1413	0.3280	0.4852	0.057*
H7B	0.1572	0.3661	0.5954	0.057*
C8	0.2770(3)	0.2783(2)	0.5783(3)	0.0445(10)
H8A	0.3414	0.2953	0.6302	0.053*
H8B	0.2225	0.2419	0.6106	0.053*
O4	0.3341(2)	0.24242(13)	0.49762(16)	0.0392(6)
C9	0.3971(3)	0.1748(2)	0.5307(3)	0.0437(10)
H9A	0.3359	0.1347	0.5423	0.052*
H9B	0.4463	0.1843	0.5954	0.052*
C10	0.4814(3)	0.14978(19)	0.4509(2)	0.0411(9)
H10A	0.5149	0.0991	0.4681	0.049*
H10B	0.4336	0.1465	0.3843	0.049*
N2	0.5828(3)	0.20283(17)	0.4444(2)	0.0366(8)
H2	0.625(3)	0.2010(18)	0.500(2)	0.044*
C11	0.6684(3)	0.18081(19)	0.3684(2)	0.0402(10)
H11A	0.6215	0.1718	0.3026	0.048*
H11B	0.7109	0.1333	0.3896	0.048*
C12	0.7631(3)	0.2419(2)	0.3565(3)	0.0412(10)
H12A	0.8004	0.2572	0.4239	0.049*
H12B	0.8301	0.2229	0.3159	0.049*
C13	0.3113(3)	0.29258(19)	0.1439(3)	0.0360(9)
C14	0.3567(3)	0.3535(2)	0.0906(2)	0.0366(9)
C15	0.2813(3)	0.4169(2)	0.1046(3)	0.0364(9)
C16	0.1884(3)	0.39450(19)	0.1681(3)	0.0353(9)
C17	0.2064(3)	0.31836(19)	0.1926(2)	0.0350(9)
C18	0.3655(3)	0.21497(19)	0.1515(3)	0.0477(10)
H18A	0.3195	0.1850	0.1963	0.072*
H18B	0.3612	0.1921	0.0855	0.072*
H18C	0.4504	0.2180	0.1775	0.072*
C19	0.4695(3)	0.3515(2)	0.0262(3)	0.0499(10)
H19A	0.5000	0.2996	0.0224	0.075*
H19B	0.5351	0.3838	0.0574	0.075*
H19C	0.4454	0.3699	−0.0423	0.075*
C20	0.2902(3)	0.4927(2)	0.0539(3)	0.0535(11)
H20A	0.2911	0.5326	0.1053	0.080*
H20B	0.2186	0.4997	0.0053	0.080*
H20C	0.3666	0.4950	0.0183	0.080*
C21	0.0851(3)	0.44569(19)	0.1991(3)	0.0496(11)
H21A	0.1198	0.4947	0.2206	0.074*
H21B	0.0444	0.4226	0.2555	0.074*
H21C	0.0244	0.4529	0.1414	0.074*
C22	0.1287(3)	0.27075(19)	0.2596(3)	0.0434(10)
H22A	0.0792	0.3038	0.3004	0.065*
H22B	0.1833	0.2395	0.3046	0.065*
H22C	0.0734	0.2382	0.2171	0.065*

of $ZnCp^*_2$. The title compound has been obtained as a crystallized product of a partial metathesis reaction, while the remaining ingredients, Zn^{2+} cations as well as $[Si_4]^{4-}$ and $[Si_9]^{4-}$ cluster anions, were not found as parts of crystalline phases after this experiment.

[Rb(diaza-18-crown-6)]Cp* crystallizes in space group $P2_1/c$ with all atoms at general positions. The Rb^+ cation is coordinated by one diaza-18-crown-6 molecule and one Cp* anion. While pure RbCp* is found to crystallize in polymeric "multidecker" strands [10], here the presence of the crown ether causes the formation of molecular units, similar to the effect of 18-crown-6 on RbCp* in THF [11]. The Rb^+ cation is situated near the centre of the diaza-18-crown-6 molecule but apart from the ring plane shifted in direction of the Cp* anion as previously found for [Rb(diaza-18-crown-6)] complexes in Fulleride salts [12]. Rb is bound to the Cp* ligand *via* two short Rb—C bonds of 3.075(3) Å and 3.210(3) Å which are in the same range as those observed for the η^5 coordination in [Rb(18-crown-6)]Cp* [11]. All atoms of the Cp* ligand are in plane and the cyclopentadienyl ring is a nearly perfect pentagon (C—C bond lengths between 1.398(4) Å and 1.418(4) Å, C—C—C angles between 107.3(3)° and 108.8(3)°) which differs clearly from the shape of the neutral Cp*–H molecule [13], suggesting that the negative charge is located at Cp*. Confirming the neutral nature of the diaza-18-crown-6 molecule, one H atom close to each N atom could have been located from the Fourier map. In contrast to the structure of the free diaza-18-crown-6 molecule [14], where the N—H bonds are parallel, both the N—H bonds of the [Rb(diaza-18-crown-6)] complex are directed almost perpendicular to the ring plane. Probably the orthogonal N—H bond hampers the formation of the symmetric η^5 coordination, possibly by forming N—H···C hydrogen bonds instead.

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