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Structural characterization of the columnar alkali metal cyclopentadienide $[K\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}]_\infty$ †

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Unsolvated 1,2,4-tris(trimethylsilyl)cyclopentadienyl potassium ($K[Cp^{3Si}]$) crystallizes as a base-free "super-sandwich" of alternating potassium ions and Cp′ rings. The polymeric chains in the structure are not connected as in other unsolvated KCp′ structures, but uniquely consist of independent columns. This type of structure has previously been observed in base-free lithium cyclopentadienyl complexes; however, $K[Cp^{3Si}]$ is the first base-free potassium cyclopentadienyl complex that crystallizes without interactions between neighboring chains.

Introduction

The cyclopentadienyl ring and its substituted derivatives are by far the most widely used ligands in contemporary organometallic chemistry.[1] Their alkali metal salts are common reagents for incorporating them into metal complexes, yet solid state structural information for Group 1 cyclopentadienides is comparatively limited.[2] Particularly interesting are the base-free species, since coordinating solvents can effect dramatic changes in their structures. Many base-free alkali metal cyclopentadienides have low solubility in non-coordinating solvents, however, and single crystals large enough for X-ray analysis are often difficult to obtain. Powder X-ray diffraction has been used to solve the structures of the parent species MCp (M = Li–K,[3] Rb,[4] Cs[5]), but only two single crystal structures of unsolvated, ring-substituted alkali metal cyclopentadienides [$Li\{C_5H_4(SiMe_3)\}$[6] and $K\{C_5H_4(SiMe_3)\}$[7]] have been reported.

Potassium cyclopentadienyl complexes are particularly useful precursors in the synthesis of organo-alkaline earth complexes.[8] In these systems, the low solubility of potassium salts in organic solvents allows for straightforward separation of halide byproducts from the desired heavy alkaline-earth (Ca, Sr, Ba) cyclopentadienyl compounds. The use of $K[Cp^{3Si}]$ [1,2,4-tris(trimethylsilyl)cyclopentadienyl potassium] has made possible the isolation of previously inaccessible types of complexes of calcium, strontium and barium;[9] in our work with this precursor, X-ray quality crystals of $K[Cp^{3Si}]$ were obtained that permitted the determination of its solid state structure.

Results and discussion

Crystals of 1,2,4-tris(trimethylsilyl)cyclopentadienyl potassium form extremely thin fibers when slowly grown from a saturated THF–toluene solution. Although solvent coordination to alkali metal cyclopentadienides is common,[3] the crystals in this case are base-free. Presumably the tight packing of the potassium ions and the heavily substituted cyclopentadienyl rings (see below) precludes additional coordination of ethers or aromatics. A colorless crystal measuring only 20 µm by 20 µm in thickness was used to obtain the X-ray crystal structure.

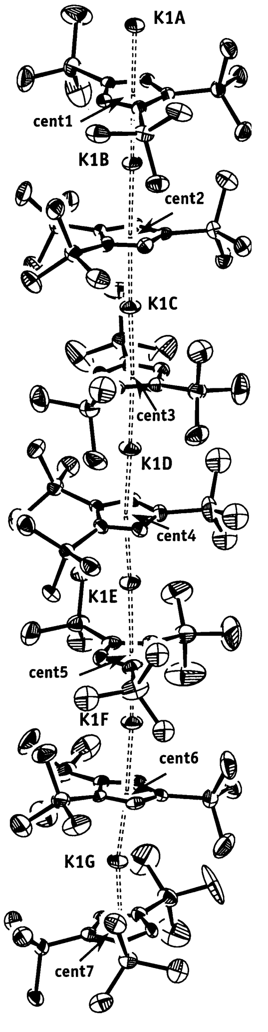

Fig. 1 ORTEP diagram of the non-hydrogen atoms of the asymmetric unit of $[K\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}]_\infty$, giving the labeling scheme used in Table 1. Thermal ellipsoids are shown at the 30% level.

The basic structural motif consists of potassium coordinated to an η^5-Cp^{3Si} ring; this unit repeats with random ring orientations to form nearly linear polymeric chains. The crystal-

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† Dedicated to the memory of Professor Ronald Snaith, a colleague and friend.

Table 1 Selected bond distances (Å) and angles (°) for $[K\{C_5H_2(SiMe_3)_3\}]_\infty$

K(1A)–Cent(A)	2.710	K(1A)–K(1B)–K(1C)	173.77
K(1B)–Cent(A)	2.765	K(1B)–K(1C)–K(1D)	178.71
K(1B)–Cent(B)	2.763	K(1C)–K(1D)–K(1E)	174.58
K(1C)–Cent(B)	2.750	K(1D)–K(1E)–K(1F)	173.82
K(1C)–Cent(C)	2.749	K(1E)–K(1F)–K(1G)	173.48
K(1D)–Cent(C)	2.762	K(1F)–K(1G)–K(1A)′	171.60
K(1D)–Cent(D)	2.765	K(1A)–Cent(A)–K(1B)	179.15
K(1E)–Cent(D)	2.772	K(1B)–Cent(B)–K(1C)	177.26
K(1E)–Cent(E)	2.770	K(1C)–Cent(C)–K(1D)	174.20
K(1F)–Cent(E)	2.756	K(1D)–Cent(D)–K(1E)	173.54
K(1F)–Cent(F)	2.752	K(1E)–Cent(E)–K(1F)	174.52
K(1G)–Cent(F)	2.747	K(1F)–Cent(F)–K(1G)	176.39
K(1G)–Cent(G)	2.736	K(1G)–Cent(G)–K(1A)′	178.03
K(1A)′–Cent(G)	2.723	Cent(A)–K(1B)–Cent(B)	172.97
		Cent(B)–K(1C)–Cent(C)	177.20
Cent(E)–K(1F)–Cent(F)	174.15	Cent(C)–K(1D)–Cent(D)	171.73
Cent(F)–K(1G)–Cent(G)	168.91	Cent(D)–K(1E)–Cent(E)	171.42

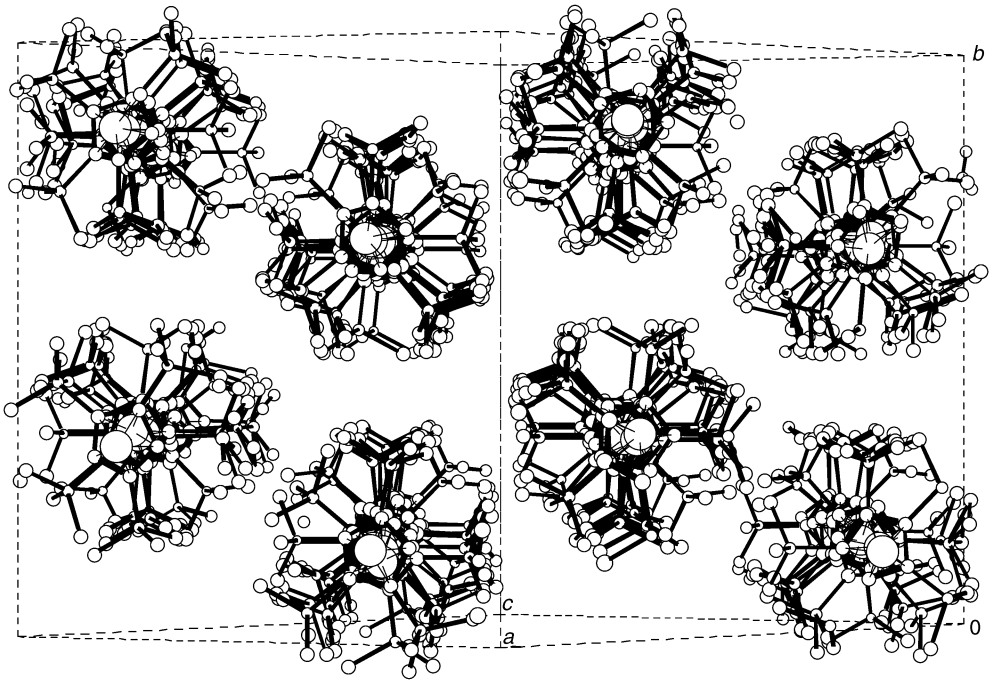

Fig. 2 Packing diagram of $[K\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}]_\infty$ viewed in a projection, normal to the [−1 0 1] plane.

lographic asymmetric unit is a "super-sandwich" stack of seven alternating potassium ions and $[Cp^{3Si}]^-$ rings (Fig. 1). Selected bond distances and angles of the complex are listed in Table 1.

The chains in $K[Cp^{3Si}]$ are packed as independent columns without side-by-side interactions between neighboring shafts (Fig. 2); the closest intercolumn Me···Me′ distance is 3.93 Å. In contrast, the only other base-free structures of KCp′ complexes feature connections between adjacent polymeric chains. KCp itself consists of a three-dimensional salt-like array of Cp^- and K^+ ions (Fig. 3).[3] The addition of one trimethylsilyl substituent to the ring breaks this array into two-dimensional sheets of interacting chains, as observed in the structure of $K[Cp^{Si}]$ (trimethylsilylcyclopentadienyl potassium) (Fig. 3).[7] The addition of two more trimethylsilyl groups to each ring blocks all side interactions, leaving only independent chains in $K[Cp^{3Si}]$.

At the time the structure of $K[Cp^{Si}]$ was reported,[7] it was suggested (correctly) that the steric bulk of the additional trimethylsilyl groups in $K[Cp^{3Si}]$ would block interactions between the K–Cp′–K–Cp′ stacks, but (incorrectly) that the presence of such interactions was critical to the formation of stable crystals. Since that time, both the structure of $Li[Cp^{Si}]$, which also consists of independent columns,[6] along with this work have demonstrated that such connections between the polymeric

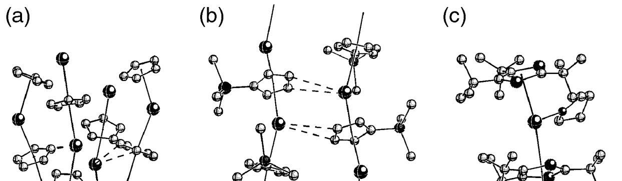

Fig. 3 (a) The interactions between a set of four columns in the three-dimensionally linked $\{K[C_5H_5]\}_\infty$; (b) the interactions between neighboring chains in the two-dimensionally linked $[K\{C_5H_4(SiMe_3)\}]_\infty$; (c) the independent columns of $K[P_2C_3Bu^t_3]_\infty$.

chains are not necessary for the crystallization of a base-free Group 1 cyclopentadienyl complex.

The near linearity of potassium atoms in **1** (K–K′–K″ angles range from 171.6 to 178.7°) contrasts with that seen in the three- and two-dimensionally linked columns of KCp (K–K′–K″ angle of 138.0°)[3] and K[Cp^{Si}] (K–K′–K″ angle of 150.7°).[7] The intercolumn interactions between the Cp rings and potassium in KCp and K[Cp^{Si}] create bending that is not observed in the independent chains of K[Cp^{3Si}]. It should be noted that with the smaller lithium ion, linear or nearly linear chains can be produced with less heavily substituted rings. The LiCp structure itself consists of linear chains (Li–Li′–Li″ angle of 180°),[3] and the Li–Li′–Li″ angle in Li[Cp^{Si}] is nearly linear at 174.5°.[6] More complete substitution of the cyclopentadienyl ring is required to prevent the larger metal center of potassium from coordinating to neighboring ligands.

Although the effects of alkyl substitution on cyclopentadienyl ligands have been extensively studied,[2] less information is available concerning the contributions of silyl substituents to the structure of cyclopentadienyl metal complexes. Successive trimethylsilyl substitution in TMEDA-solvated lithium cyclopentadienyl complexes results in elongation of the Cp–Li bonds; however, *ab initio* calculations did not reproduce this elongation with increased silyl substitution.[2] Harder has suggested that the observed elongation is likely due to steric interactions between the TMEDA coordinated to lithium and the trimethylsilyl substituents; the observed lengthening of the Li–N(TMEDA) bonds in these complexes also agrees with this explanation. The unsolvated potassium examples confirm this suggestion, as there is no elongation upon increasing the number of silyl groups in the unsolvated KCp′ structures. The K–C(ring) distances in K[Cp^{Si}] range from 2.933 to 3.101 Å (average 3.01 Å); this is equivalent to the average K–C(ring) distances of 3.06 Å [2.955(5)–3.140(6) Å, η^5-Cp ring only] in KCp[3] and 3.03 Å (2.988–3.079 Å) in K[Cp^{Si}].[7]

The steric effect of three bulky groups on a five-membered ring is so dominating that the ring need not be all-carbon, nor does the metal need to be base-free, in order to obtain independent columns of rings and metal ions. This is illustrated in the structure of K[$P_2C_3Bu^t_3$] (Fig. 3), which has separated stacks of potassium ions and P_2C_3 rings.[10] The K–K′–K″ angle varies from 148.4 to 154.2°; the ring centroid–K–ring centroid angles range from 150.0 to 170.9°.

Experimental

General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high-vacuum, Schlenk, or drybox techniques. Proton (^{1}H) NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 MHz and were referenced to the residual resonances of THF-d_8 (δ 3.58).

Materials

K[N(SiMe$_3$)$_2$] was purchased from Aldrich and used as received. 1,2,4-Tris(trimethylsilyl)cyclopentadiene was prepared using literature procedures.[11] Solvents for the reaction were distilled under nitrogen from sodium or potassium benzophenone ketyl. The NMR solvent was vacuum distilled from Na/K (22/78) alloy.

Synthesis of K[$C_5H_2(SiMe_3)_3$-1,2,4] from $C_5H_3(SiMe_3)_3$-1,2,4 and K[N(SiMe$_3$)$_2$]. $C_5H_3(SiMe_3)_3$-1,2,4 (2.53 g, 8.95 mmol) and K[N(SiMe$_3$)$_2$] (1.78 g, 8.91 mmol) were added to 50 mL of toluene in a 125 mL flask. The reaction was stirred overnight, during which time a white precipitate formed. The precipitate was collected by filtration of the reaction mixture through a glass frit, and dried under vacuum to give K[$C_5H_2(SiMe_3)_3$-1,2,4] (2.41 g, 84%) as an off-white powder, identified from its ^{1}H NMR spectrum (THF-d_8; 20 °C): δ 6.47 (s, 2H, ring-CH), 0.20 [s, 9H, Si(CH$_3$)$_3$], 0.14 [s, 18H, Si(CH_3)$_3$].

Crystal structure determination of K[$C_5H_2(SiMe_3)_3$-1,2,4]. Crystals for X-ray analysis were grown by slow evaporation of a saturated THF–toluene solution at room temperature. A colorless, very small needle (0.20 × 0.02 × 0.02 mm) of the sample was placed onto the tip of a 0.1 mm glass capillary and mounted on a Bruker SMART system for data collection at 173(2) K. Data collection and structure solution were conducted at the X-Ray Crystallography Laboratory at the University of Minnesota. The intensity data were corrected for absorption (SADABS[12]). The structure was solved using SHELXS-86[13] and refined using SHELXL-97.[14] Most of the non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon atoms of the two disordered trimethylsilyl groups were modeled as spheres. In addition to those, carbon atoms belonging to some of the trimethylsilyl groups displayed large thermal displacement parameters. In these cases, no other major sites could be refined. The large ellipsoids should be understood as models for thermal movement and disorder over multiple sites. The data (observed) to parameter ratio is relatively low (6 : 1), which is due to the weak scattering of the very small specimen measured.

Crystal data. $C_{98}H_{203}K_7Si_{21}$, $M = 2245.19$, monoclinic, space group $P2_1/c$ (no. 14), $a = 31.796(2)$, $b = 21.666(2)$, $c = 21.289(2)$ Å, $\beta = 90.496(2)°$, $U = 14664.7(15)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 4.12 cm^{-1}, 88 344 reflections measured, 25 831 unique, 6969 with $I > 2\sigma(I)$ used in calculations. The final $R(F^2)$ was 0.0592; $wR(F^2)$ was 0.1145.

CCDC reference number 154073.

See http://www.rsc.org/suppdata/dt/b0/b009359i/ for crystallographic data in CIF or other electronic format.

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