Silicone Grease as a Precursor to a Pseudo Crown Ether Ligand: Crystal Structure of $[K^+]_3[K(Me_2SiO)_7{}^+][InH(CH_2CMe_3)_3{}^-]_4$

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The crystallization of $K[InH(CH_2CMe_3)_3]$ from heptane in the presence of silicone grease led to the formation of the title compound, in which one potassium cation is surrounded by a planar cyclo-$(Me_2SiO)_7$ ligand; $K^+\cdots O$ distances range from 2.86(3) to 2.99(4) Å.

We have previously reported the preparation of $K^+[InH(CH_2CMe_3)_3{}^-]$ along with a crystallographic study of the related dinuclear species $K^+[H\{In(CH_2CMe_3)_3\}_2{}^-]$.[1] Attempts to crystallize $K^+[InH(CH_2CMe_3)_3{}^-]$ from pentane at low temperature produced large, colourless, transparent, rectangular crystals in the mother liquor. When the pentane was removed, the crystals became opaque and shattered. In an attempt to protect the material from solvent loss, the following crystallization procedure was used. A sample of $K^+[InH(CH_2CMe_3)_3{}^-]$ and a small amount of Dow Corning high-vacuum silicone grease (intended to protect any crystals thus grown) were placed in a tube equipped with a Solv-Seal joint. Heptane was added by vacuum distillation. The solid dissolved as the mixture was warmed from −196 °C to room temp. over 2 h. Needle shaped single crystals formed overnight. The crystal used for the X-ray crystallographic study was cut from a larger crystal and mounted in a thin-walled capillary tube. [*N.B.* All materials were handled under purified argon or *in vacuo*. Organoindium hydrides are extremely air- and moisture-sensitive.]

The completed X-ray diffraction study[†] shows the crystals to have the composition $[K^+]_3[K(Me_2SiO)_7{}^+][InH(CH_2CMe_3)_3{}^-]_4$. The overall structure is shown in Fig. 1. The 'bare' potassium cations are associated with the cavity between the $[InH(CH_2CMe_3)_3]^-$ ions and interact with hydrogen atoms on various neopentyl groups.

The totally unexpected feature of the structure is the presence of the $(Me_2SiO)_7$ moiety, which acts as a pseudo crown ether ligand around atom K(1); see Fig. 2. Although the structure as a whole is of poor quality, all features of this system are unequivocal. The $(Me_2SiO)_7$ moiety is based upon an essentially planar 14-membered Si_7O_7 ring of approximately D_{7h} symmetry. The potassium ion, defined by K(1), is coplanar with this ring and interacts with all seven oxygen atoms of the cyclopolysiloxane ($K^+\cdots O$ = 2.86(3)–2.99 (4) Å, average = 2.93 Å). Silicon–oxygen distances are 1.54(4)–

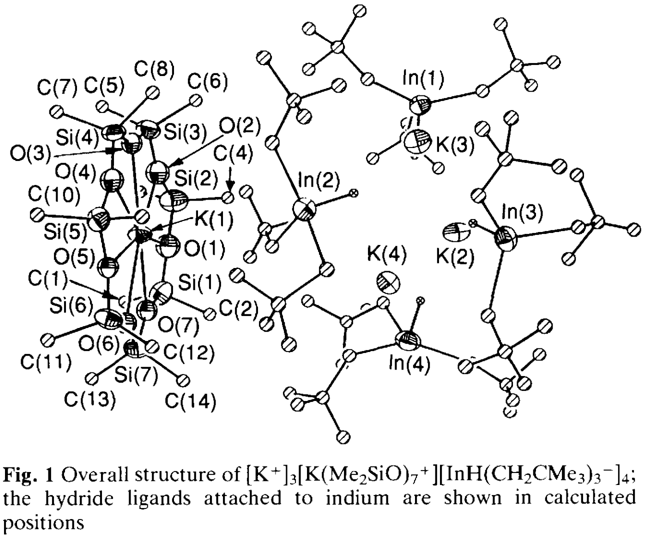

Fig. 1 Overall structure of $[K^+]_3[K(Me_2SiO)_7{}^+][InH(CH_2CMe_3)_3{}^-]_4$; the hydride ligands attached to indium are shown in calculated positions

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[†] *Crystal data*: $C_{74}H_{178}In_4K_4O_7Si_7$, colourless, M = 1992.5, monoclinic, $P2_1/n$; a = 14.704(2), b = 24.195(3), c = 32.759(6) Å, β = 93.674(12)°, V = 11631(3) Å^3, Z = 4, T = 298 K, D_c = 1.138 g cm^{-3}, μ(Mo-Kα) = 1.02 mm^{-1}, $F(000)$ = 4192. Of 16437 data collected (2θ = 5–45°), 15243 were independent, but only 3191 were observed ($6\sigma F_o$). Data were corrected for absorption. The data set is extremely weak [average value of $I/\sigma(I)$ is 5.29] and there is disorder in certain of the neopentyl ligands. Final R = 9.85%. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

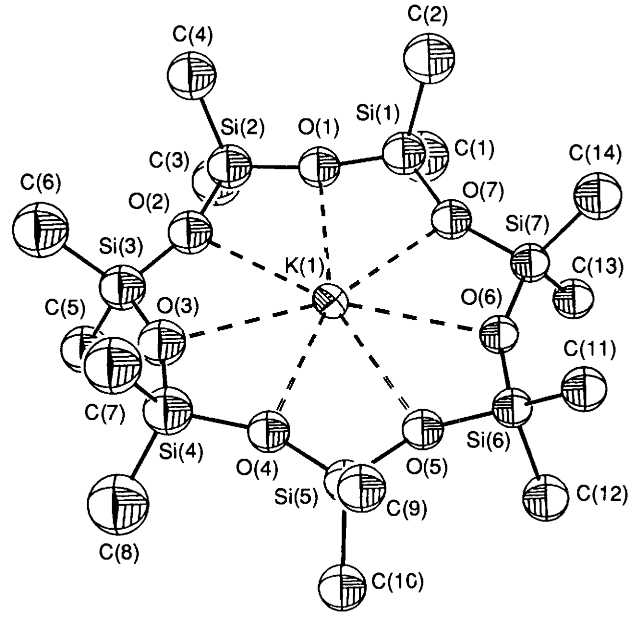

Fig. 2 The K(Me$_2$SiO)$_7^+$ moiety. Distances of interest (Å): K(1)···O(1) = 2.99(4), K(1)···O(2) = 2.94(5), K(1)···O(3) = 2.93(3), K(1)···O(4) = 2.93(4), K(1)···O(5) = 2.86(3), K(1)···O(6) = 2.94(3), K(1)···O(7) = 2.94(4)

1.67(4) Å (average = 1.61 Å) and silicon–carbon distances are 1.78(7)–1.99(12) Å (average = 1.88 Å).

Cyclopolydimethylsiloxanes, (Me$_2$SiO)$_n$ have been known for some time. The physical properties of the trimer up to the octamer were described about 50 years ago.[2] Individual species up to at least the tetracontamer (n = 40) have since been isolated.[3] An electron diffraction study[4] showed that the trimer, (Me$_2$SiO)$_3$, had a planar six-membered ring.[4] An X-ray diffraction study[5] of the tetramer, (Me$_2$SiO)$_4$, and a partial X-ray diffraction study[6] of the octamer, (Me$_2$SiO)$_8$, showed them to have puckered rings. Electron diffraction studies on the tetramer, pentamer and hexamer[7] also indicated puckered (SiO)$_n$ rings. IR and Raman spectra of both liquid and solid (Me$_2$SiO)$_7$ suggest that each contains a number of conformers;[8] this, too, suggests a puckered ring. The D_{7h} symmetry exhibited by the (Me$_2$SiO)$_7$ ligand in the present structural study is clearly a result of its coordination to the potassium cation.

A search of *Chemical Abstracts* and secondary review sources[9] (at the behest of a referee) revealed no other example of a cyclopolysiloxane behaving as a crown ether. Indeed, a paper entitled (in translation) 'Study of the Possibility of using Cyclodimethylsiloxanes as "Crown Compounds"' showed that neither (Me$_2$SiO)$_7$ nor (Me$_2$SiO)$_8$ was efficacious as a crown ligand towards the Na$^+$ cation.[10]

The derived structure leads to some interesting questions.

(1) Why is the heptameric cyclopolysiloxane, (Me$_2$SiO)$_7$, specifically found in the crystals? It seems probable that it is formed by reaction of silicone grease with [K$^+$][InH(CH$_2$CMe$_3$)$_3^-$]. Silicone grease consists principally of polydimethylsiloxane (>80%), dimethylcyclosiloxane (< 1%, ring size unknown) and hydroxy terminated dimethylsiloxane (~5–10%).[11] The cyclic heptamer is not even a specifically identified component of silicone grease.

(2) Is it possible to isolate different sized cyclic oligomers, (Me$_2$SiO)$_n$, from silicone grease based upon the size of the cation (M$^+$) in M$^+$[InH(CH$_2$CMe$_3$)$_3^-$]?

(3) Can various (Me$_2$SiO)$_n$ species be widely used as crown ether ligands?

Finally, the results shown herewithin indicate that silicone grease cannot always be considered as an innocuous inert material, but can participate as a reactant.

Further work is in progress, including a structural study on a triclinic crystal modification of the present structure.

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