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A K_3-Containing Trigonal-Bipyramidal Cluster: Synthesis of $(KSCN)_3{\cdot}5HMPA$ by Reaction of Solid NH_4SCN with Solid K or KH in Toluene/HMPA and Its Crystal Structure Revealing a Triangle of Three K^+ Ions Linked by Three Equatorial μ_2-HMPA Ligands and Bicapped by Two μ_3-HMPA Ligands

We have previously reported a versatile route to anhydrous lithium complexes of type $(LiX{\cdot}xL)_n$, with X = Cl, Br, I, or SCN and with L (Lewis bases) = HMPA [$O{=}P(NMe_2)_3$], TMEDA, or PMDETA, by reacting solid ammonium salts, NH_4X, with Bu^nLi solution in toluene containing stoichiometric amounts of L.[1] More recently, several of these so-synthesized complexes have been shown to adopt novel structures, most notably, $(LiNCS{\cdot}TMEDA)_\infty$, a 1-D polymer,[2] $(LiBr)_2{\cdot}3HMPA$, consisting of two LiBr monomers bridged by μ_2-HMPA ligands,[3] and $(LiNCS{\cdot}2HMPA)_2$, an asymmetric dimer of form $(HMPA)_2Li(\mu_2\text{-}HMPA)_2Li(NCS)_2$.[4] Here we report a two-way extension of the above: from lithium to potassium and from using, as the metal source, a solution of an organometallic compound (Bu^nLi) to using *solids*, and moreover decidedly *inorganic* ones. Thus, it is shown that solid NH_4SCN reacts with solid K metal or with solid KH in toluene/HMPA media to give $(KNCS)_3{\cdot}5HMPA$ (**1**). An X-ray diffraction study reveals unprecedented structural features, **1** consisting of a triangle of K^+ ions (cf. the M or M_2 units found above when M = Li) attached to the N ends of three exo NCS^- anions, bridged in the equatorial plane by three μ_2-HMPA ligands, and then capped, above and below, by two μ_3-HMPA ligands.

Potassium metal (0.39 g, 10 mmol) was added to solid NH_4SCN (0.76 g, 10 mmol) suspended in toluene (10 mL) and HMPA (3.58 g, 20 mmol),[5] under nitrogen and at room temperature. An immediate reaction occurred, with gas evolution and development of a green color in the liquid. After ca. 5 min this color began to fade, with concomitant production of a white precipitate. Careful warming of the mixture accelerated this process so that, within 15 min, no potassium metal remained. The white solid was dissolved by addition of toluene/hexane (10 mL/25 mL) and of further HMPA (5.37 g, 30 mmol). Refrigeration then gave colorless crystalline needles, identified as $(KSCN)_3{\cdot}5HMPA$ (**1**).[6]

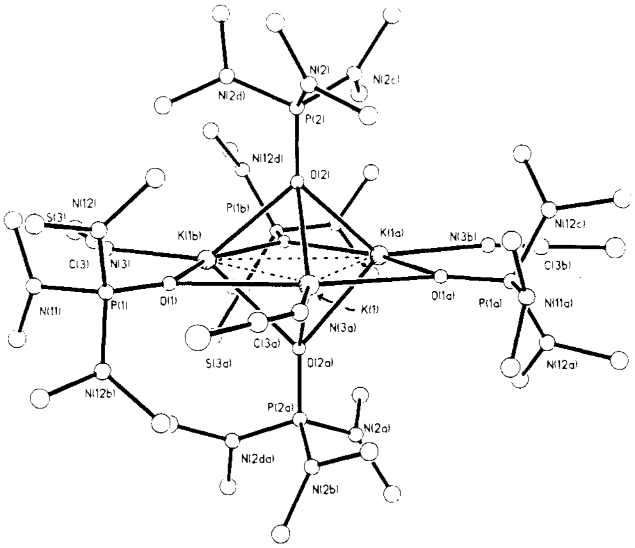

Figure 1. A PLUTO plot of the molecular structure of $(KNCS)_3{\cdot}5HMPA$ (**1**). Methyl hydrogen atoms have been omitted for clarity; dashed lines between K^+ ions have been inserted to give perspective and have no structural or bonding implications.

The same product is formed, in similarly high yield (90%), by reacting KH solid with NH_4SCN solid in HMPA (1:1:5) and toluene; as in the metal route, the vigorous reaction proceeds through colored (here, turquoise) intermediates.

The stoichiometry of **1** hinted at an unusual structure, as did the (so far, unexplained) closeness of the HMPA doublet in its ^1H NMR spectrum[6] (0.03 ppm; cf. ~0.10–0.12 ppm in HMPA itself and in previous HMPA-complexed lithium species). An X-ray diffraction study[7] has now shown that **1** does indeed have an unprecedented solid-state structure, as illustrated in Figure 1. It consists of a $(K^+)_3$ triangle whose K···K edges [length 3.655 (4) Å; K^+ ionic radius ~1.4 Å] are bridged in this equatorial plane by three μ_2-HMPA ligands [K–μ_2-O distance 2.748 (8) Å]; the metal triangle is then capped, above and below, by two μ_3-HMPA ligands [K–μ_3-O distance 2.712 (5) Å], and each K^+ reaches formal pentacoordination by exo contacts to a thiocyanate anion [K–N distance 2.690 (12) Å].

Comparisons of **1** with other potassium-containing structures (or with alkali-metal ones in general) are difficult. A literature search[8] reveals some 45 structurally characterized KSCN com-

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[1] Barr, D.; Snaith, R.; Wright, D. S.; Mulvey, R. E.; Wade, K. *J. Am. Chem. Soc.* **1987**, *109*, 7891. The paper notes the advantages of this in situ route and the likely applications of these complexes; the route is under patent (European Patent No. 88309913.7) filed by the Associated Octel Co. Ltd.

[2] Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1988**, 145.

[3] Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318.

[4] Barr, D.; Doyle, M. J.; Drake, S. R.; Raithby, P. R.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1415.

[5] HMPA is a cancer suspect agent and should be treated with extreme care.

[6] For **1**: yield 3.51 g, 89% with respect to K metal taken; mp from 60 °C. ^1H NMR spectrum (C_6D_6, 250 MHz): HMPA $^{31}P\{^1H\}$ doublet, δ 2.44, 2.41 ppm. Anal. ($C_{33}H_{90}K_3N_{18}O_5P_5S_3$): C, H, K, N, P.

[7] Crystal data for **1**: $(KSCN)_3{\cdot}5HMPA$, $C_{33}H_{90}K_3N_{18}O_5P_5S_3$, M_r = 1187.56, hexagonal, $P6_3/m$ (No. 176), a = 16.354 (3) Å, c = 14.061 (6) Å, V = 3257 Å^3, Z = 2 trimers, R = 0.099 and R_w = 0.119 for 1291 unique observed reflections at T = 235 K (2θ range 5–116°, Cu Kα radiation).

[8] Search of the Cambridge Crystallographic Data Base. Director: Dr. O. Kennard, University of Cambridge, Cambridge, U.K.

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plexes, but all with macrocyclic, crown-type ligands (so giving, usually, single K^+ units); any bonding $K^+\cdots NCS^-$ contacts are typically of length 2.8-3.0 Å. Perusal of a recent review of organometallic compounds containing heavier alkali metals (Na-Cs)[9] has also failed to find a structure comparable with that of **1**. Some comment can, though, be made concerning this structure; cf. that of $(LiNCS{\cdot}2HMPA)_2$.[4] The ionic radii of (six-coordinate) Li^+ and K^+ differ by about 0.62 Å, so that the M-N distances (2.007 Å in the Li complex, ~0.69 Å longer when M = K, in **1**) and the M-μ_2-O distances (of HMPA; 2.015 Å in the Li complex, ~0.74 Å longer in **1**) only roughly fall in line. Within the thiocyanate anions of the two complexes, there is better agreement (N-C and C-S distances in the Li complex being 1.156 and 1.629 Å, respectively, and in **1** being 1.142 (16) and 1.625 (12) Å, respectively), enabling their formulation as

$$[\mathrm{N}\overset{\cdots}{=}\mathrm{C}\overset{\cdots}{-}\mathrm{S}]^-$$

For the M^+-μ_3-O (of HMPA) coordinations, there are seemingly no precedents in alkali-metal chemistry. Even though each $(Me_2N)_3P{=}O$ ligand has just two lone pairs formally available for bonding to, one supposes, just two metal centers, the $\mathrm{O}\overset{\cdots}{-}\mathrm{P}$ distances within the μ_2 and μ_3 ligands of **1** show no significant difference [being 1.473 (9) and 1.491 (8) Å, respectively], which could be attributed to use of π-electron density in the latter case.

Clearly, **1** has a highly ionic structure. It can be viewed as a bicapped $(K_3O_3)^{3+}$ hexagon [see Figure 1, looking along O(1)-K(1)-O(1a); angles at K 156.6 (2)°] or as a $(K_3)^{3+}(\mu_3\text{-HMPA})_2$ trigonal bipyramid whose $K^+\cdots K^+$ edges are stitched (borane-like) by μ_2-HMPA ligands. Either way, the equatorial belt is pulled out, presumably to maximize $K^+\cdots K^+$ distances.

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Supplementary Material Available: Details of the crystal structure determination, Tables S1-S4, listing final atomic coordinates, bond lengths, bond angles, and thermal parameters, and a view of the unit cell contents showing the two trimeric molecules of **1** (6 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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[9] Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169.

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Tris(trimethylsilyl)silyl Derivatives of Tri-*tert*-butoxyzirconium and Tri-*tert*-butoxyhafnium. X-ray Crystal Structure of $(Me_3CO)_3ZrSi(SiMe_3)_3$

Recent investigations in our laboratory have focused on the formation and reactivity of early-transition-metal-silicon bonds.[1] Studies with d^0 zirconium and hafnium derivatives such as $Cp_2M(SiMe_3)Cl$ (Cp = η^5-C_5H_5),[2] $Cp_2M[Si(SiMe_3)_3]Cl$,[2c] $Cp^*{}_2Zr(SiHMes_2)Cl$ (Cp* = η^5-C_5Me_5; Mes = 2,4,6-$Me_3C_6H_2$),[3] $Cp^*Cl_2MSi(SiMe_3)_3$,[4] and $CpCp^*M[Si(SiMe_3)_3]Cl$[1c,5] have shown that these metal-silicon bonds are unusually reactive toward a variety of substrates. A common feature of these silyl compounds is the presence of cyclopentadienyl (C_5H_5 or C_5Me_5) ancillary ligands. Because the reactivity of early-transition-metal-silicon bonds is dramatically influenced by substituent effects at both the transition metal and silicon,[1c,2c,3,5] we have sought syntheses of early-transition-metal-silyl complexes with different ligand environments. We now report the synthesis of complexes $(Me_3CO)_3MSi(SiMe_3)_3$ (**1**, M = Zr; **2**, M = Hf), which to our knowledge are the first group 4 silyl derivatives that do not contain cyclopentadienyl ligands.

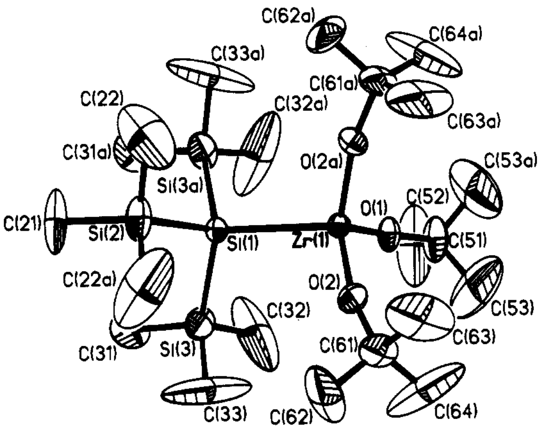

Figure 1. ORTEP view of $(Me_3CO)_3ZrSi(SiMe_3)_3$ (**1**) with thermal ellipsoids drawn at the 20% probability level. Important bond lengths (Å) and angles (deg) are as follows: Zr(1)-Si(1) = 2.753 (4), Zr(1)-O(1) = 1.90 (1), Zr(1)-O(2) = 1.884 (7); Si(1)-Zr(1)-O(1) = 107.5 (3), Si(1)-Zr(1)-O(2) = 107.7 (2), O(1)-Zr(1)-O(2) = 110.9 (3), Si(2)-Si(1)-Zr(1) = 110.7 (2), Si(3)-Si(1)-Zr(1) = 110.2 (1), Zr(1)-O(1)-C(51) = 165 (1), Zr(1)-O(2)-C(61) = 167.2 (8).

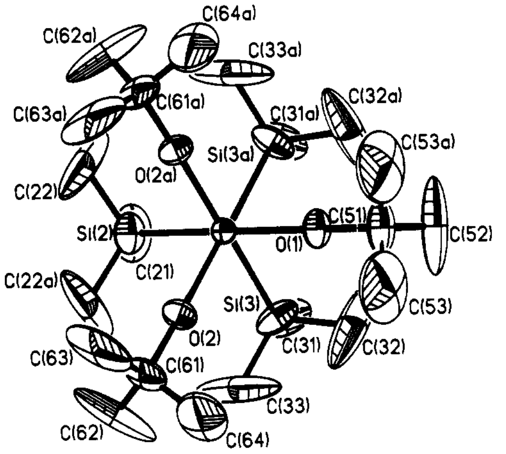

Figure 2. View of **1** down the Zr(1)-Si(1) bond.

By a modification of the literature procedure for $(CH_3CH_2CH_2CH_2O)_3MCl$,[6] the alkoxides $(Me_3CO)_3MCl$ were generated in solution by reaction of MCl_4 with 3 equiv of $M(OCMe_3)_4$[7] in diethyl ether for 12 h at 0 °C. After the solution was warmed to room temperature addition of $(THF)_3LiSi(SiMe_3)_3$[8] to this solution resulted in formation of silyl complexes **1** and **2** (reaction time 3 h), isolated in 60-70% yield by crys-

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