A Second Modification of Potassium Fluorenide and the Structure of Potassium 9-tert-Butylfluorenide: Effect of Crystallization Conditions and Substituents on Solid-State Contact Ion Pair Interactions

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Received March 18, 1993

Key Words: Potassium compounds / Fluorenide, potassium salt / Fluorenide, 9-tert-butyl, potassium salt / Solid-state organization / Polymorphism

Crystalization of potassium fluorenide or 9-tert-butylfluorenide [formed from potassium metal and fluorene or 9-tert-butylfluorene in tetramethylethylenediamine (tmeda)] from a mixture of tmeda, tetrahydrofuran (THF) and diethyl ether yields potassium bis(p-9-tert-butylfluorenyl) potassium-(tetramethylethylenediamine)-potassium bis(tetrahydrofuranyl) potassium-(tetramethylethylenediamine)-potassium (I) and red crystals of bis(tetrahydrofuranyl) potassium-(tetramethylethylenediamine)-potassium (2), both of which are highly air-sensitive. The number of solvent molecules found in the crystal structure determinations matches the integration pattern in the 'H-NMR spectrum.

The fundamental problem of determining major controlling factors in crystallization and their relative significance has become again a very active area of research. The question of „what crystallizes how and why“ is especially vivid in the discussion of the solid-state interactions of the structurally rich organoalkali metal salts. For the latter there is a growing interest in solid-state structures of the heavier congeners of lithium. The fundamental problem of determining major controlling factors in crystallization and their relative significance has become again a very active area of research. 

The structures of 1 and 2 were determined by single-crystal X-ray diffraction analysis. In 1 the potassium ion shows a π interaction with the central five-membered ring of only one pentahapto-bound fluorenyl ligand (Figure 1). The potassium-to-carbon distances (ranging from 307 to 332 pm) are longer and vary more than in (cyclopentadienyl)potassium complexes (maximal variation there 296 to 310 pm). The longer K–C contacts in 1 indicate an effective solvation of the potassium ion by the four nitrogen atoms of two chelating tmeda molecules which complete the coordination sphere around potassium and lead to the formation of a monomeric ion pair. Since the potassium ion sits on a special position (0, 1/4) along a twofold rotational
axis, the fluorenyl ligand — lying perpendicular to this axis — shows a crystallographically induced disorder, as shown in Figure 2. The disorder has been omitted in Figure 1 for clarity.

![Figure 1. Molecular structure of 1 (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; hydrogen atoms omitted). Selected distances [pm] and angles [°]: K—N1 282.4(1), K—N2 305.8(2), K—C1 332.0(4), K—C2 321.3(5), K—C7 307.1(5), K—C8' 313.2(5), K—C13' 330.5(5); N1—K—N2 61.97(5). There are no short intermolecular contacts.](image1)

![Figure 2. Crystallographically induced disorder of the fluorenyl ligand in 1 to the formula (K(p,~f,q~-tmeda)]([p-C,~H~]}. The finding of a second potential minimum in the form of the monomer modification is solely attributed to slight changes in the crystallization conditions. Crystals of the polymeric form were obtained by evaporation (ca. 12 h) of a benzene/tmeda (1:1) solution of 1[14]. The modification reported here was obtained reproducibly from a solution of 1 in more polar tmeda/THF/Et,0 (1:1:1) upon cooling. Crystals were visible after two days at -26°C. So far only electrostatic and steric factors within the contact ion pair were emphasized as being structurally decisive in comparative discussions of organoalkali compounds[12].

To the best of our knowledge, 1 represents the first example of polymorphism in an organopotassium compound[19]. Thus, caution should be exerted when discussing details such as metal solvation in crystalline organopotassium or even other alkali metal complexes. One crystal structure may not always tell the whole story of solid-state interactions, as the structure found may correspond to just one potential well, determined by external parameters such as temperature or solvent of crystallization.

(iii) Furthermore, it is interesting to note that tmeda can effectively chelate a potassium ion with the formation of an N—K—N angle of only 62°[22] (cf. the structure of 2 and ref.[7]). The large size of the potassium ion together with the given N—N distance in tmeda and an optimal "bite" angle of about 85° for the free electron pairs on the nitrogens have been given as a reason for the double-strand linkage of two potassium ions by two tmeda molecules in the polymeric modification of 1, i.e. non-formation of a K-tmeda chelate structure[42,14]. However, modeling calculations on K(en) (en = ethylenediamine) give similar energies for chelating and monodentate en[20].

The two K—N bond lengths in the monomeric allotrope of 1 differ by more than 20 pm, their average as well as the K—C distances in both polymorphic forms are, however, not significantly different[14].

![Figure 3. Section of the chain structure (along 001) of 2 in the crystal (PLUTO[37]). Selected distances [pm] and angles [°]: K1—O1 267.8(4), K1—O2 265.5(4), K1—C2 342.9(6), K1—C3 322.6(5), K1—C4 309.1(6), K1—C5 315.4(6), K1—C6 334.4(6), K1—C7 346.8(5), K1—C8 313.6(5), K1—C9 338.3(6), K1—C10 330.3(5); N1—K—N2 64.4(1). K—C contacts above 330 pm are not drawn.](image2)
The structure of 2 shows at first glance the expected zigzag-type polymeric chain structure (Figure 3) with alternating potassium and fluorenyl ions. It is remarkable, however, that the potassium is not situated above the five-membered ring, but above the aminated six-membered ring of the fluorenyl system. This ring shift is explained with the steric influence of the tert-butyl group (interaction with the solvent molecules attached to potassium). A comparative AM1 study\["\] of the fluorenyl and 9-tert-butylfluorenyl anion supports the notion of a steric origin for the haptotropic potassium shift. AM1 calculates the C-9 position somewhat less negative in the 9-tert-butyl derivative, but there is no charge transfer from the five- to the six-membered ring moiety (Figure 4). Furthermore, a comparison of the effective electrostatic potentials on the van der Waals surface (170 pm above the fluorenyl plane\[22\]; plotted in Figure 4) illustrates that there is no obvious difference between unsubstituted and 9-tert-butyl-substituted fluorenyl. Calculations suggest that energy surfaces for metal cations above a delocalized anionic ring can be quite flat, especially so for long cap-ring distances\[4,19\]. Dilithium 1,2-diphenylbenzocyclobutadiene is an example that different metal cation locations exist for the same compound\[19\].

Metal-fluorenyl six-membered ring coordination could be observed in some cases for transition metals\[15,16\]. For alkali metals such a coordination mode to fluorenyl has been observed in the structure of the tetrameric (tetracetylpropylenediamine)sodium fluorenide where a weak sixring interaction has been found together with the actual fivering coordination\[17\]. Base-free lithium fluorenide forms a dimeric unit with the lithium atoms being sandwiched between the six-membered ring planes\[23\]. Alkali metal coordination to six-membered ring entities in other extended π systems or to a phenyl group has been observed e.g. in lithium indeno-fluorene\[24\], lithium 1,1,3,3-bis(2,2’-biphenylylene)propenide\[23\], sodium terphenyl\[26\] in sodium structures with the tetraphenyllalyl anion\[27\], the 1,1,4,4-tetraphenylbutane-1,4-diyldianion\[28\], the (biphenyl-2,2-diyldiphenylethene anion\[29\], or with perylene\[30\] as well as in potassium dimethyl-phosphoniumbis(benzylide)\[31\].

The coordination sphere of the potassium ions in 2 is completed either by two THF molecules or a tmeda molecule in an alternating fashion, with the tmeda molecule again functioning as a chelate ligand. The K-C₆ distances vary between 309 and 349 pm with the shorter contacts corresponding to the K-C₅ distances in 1. In view of the longer contacts and no sharp discontinuity within the K-C₆ distances it is, however, difficult to assign a definitive coordination number to potassium.

This work was made possible by the Deutsche Forschungsgemeinschaft (Habilitation fellowship), the Fonds der Chemischen Industrie, the Freunde der TU Berlin, and the Bundesministerium für Forschung und Technologie (graduate program “Synthesis and structure elucidation of molecular compounds”). I thank Prof. H. Schumann for his generous support and Mr. R. Weimann and Mr. H. Hemling for collecting the crystallographic data sets.

**Experimental**

All operations were carried out under purified argon by using standard Schlenk and vacuum techniques. Solvents were distilled from potassium (THF) or sodium metal (tmeda) or from blue sodium/benzophenone ketyl (Et₂O).

For the assignment of the NMR chemical shifts compare ref.\[13,33\].
K(tmeda)₂/CF₃H₂O (1): 0.089 g (2.28 mmol) of potassium metal in a solution of 0.36 g (2.17 mmol) of fluorene in 10 ml of tmeda was treated for 1 h in an ultrasonic bath at 70°C. After this time, no metal could be observed anymore, and a deep brown-violet slurry had formed. Addition of 10 ml of THF and 10 ml of Et₂O gave an intensely colored but almost clear solution, and cooling to −26°C caused precipitation of I as an orange-brown crystal: 0.37 g (39%, crystal yield not optimized). — ¹H NMR (D₅THF): δ = 2.16 (s, 24H, CH₂N), 2.31 (s, 8H, CH₂N), 5.98 (br. s, 1H, 9-H), 6.58 (t, 3JHH = 7.8 Hz, 2H, 3- H), 6.95 (t, 3JHH = 7.8 Hz, 2H, 2-7H); 7.40 (d, 3JHH = 7.8 Hz, 2H, 1-8H); 7.95 (d, 3JHH = 7.8 Hz, 2H, 4-5H). — ¹³C NMR (D₅THF): δ = 46.16 (CH₃N), 58.73 (CH₂N), 83.08 (C-9), 109.86 (C-2,-7), 117.14 (C-4, -11), 149.16 (C-6, -10), 120.57 (C-3,-6), 121.68 (C-11,-12), 136.70 (C-10, -13). — C₂H₄K₂N₄ (436.7): calcd. C 72.73, H 8.33, N 4.15.

To the close proximity of two carbon centers each, because of the disorder problem. Residual electron density +0.31/-0.28 eÅ⁻³, largest residual at the tmeda molecule. Hydrogen atoms calculated for idealized positions.

AM1 Calculations: Contours and counting plots were performed with the HyperChem computational package (Version 2.0, Autodesk, Inc. Sausalito, CA 94965, USA) by using the AM1 algorithm[21] for the geometry optimization and electronic property calculation of the fluorenyl and 9-tert-butyfluorenyl anion.


Crystal Structure Determinations[34]: CAD4, Enraf-Nonius four-circle diffractometer, Mo-Kα radiation (λ = 0.71069 nm, graphite monochromator), T = 177 K, ω-2θ scan with 0.05–0.35 sin θ, scan time variable (max. 45 s). During data collection three standard reflections were periodically measured as a check of crystal stability. No significant change was observed for both compounds, reduction in intensity was less than 1%. Structure solution was performed by direct methods (SHELXLS-86). Refinement: Full-matrix least squares; non-hydrogen atoms were refined anisotropically (SHELX-76)[35].

KF(tmeda)₂/[C₃H₃N₆]: M = 436.731, crystal size: 0.3 × 0.3 × 0.4 mm. Monoclinic, space group C2/c1 (No. 15), a = 1896.2(4), b = 907.9(2), c = 1643.2(3) pm, β = 113.49(2)°, V = 259(1) pm³, Z = 4, Dcalcd = 1.118 g cm⁻³, F(000) = 952 electrons, μ(Mo-Kα) = 2.5 cm⁻¹. 5716 reflections measured (1° < 2θ < 43°), 4334 independent, 3041 observed [F > 5σ(F)], final R = 0.05, R = 1.8; 497 refined parameters, empirical absorption correction (DIFABS, max. = 1.041/min = 0.720). Residual electron density +0.44–0.31 eÅ⁻³, largest residual at the tmeda molecule. Hydrogen atoms calculated for idealized positions.
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[34] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57199, the names of the authors, and the journal citation.


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