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Coronene-Potassium(THF)$_2$(tmeda): X-Ray Structure and MNDO Calculations of a Half-Sandwich Contact Ion Pair as a Model for Potassium(Adsorbate)-Graphite Surface Interactions

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Crystallization of potassium(1+) and the radical ion coronene(1−) from a mixture of tetramethylethylenediamine (tmeda), tetrahydrofuran (THF), and diethyl ether yields a monomeric solvated ion pair **1** with potassium unsymmetrically π-coordinated to an external ring of the polyaromatic system according to an X-ray structure determination and in agreement with a MNDO theoretical investigation.

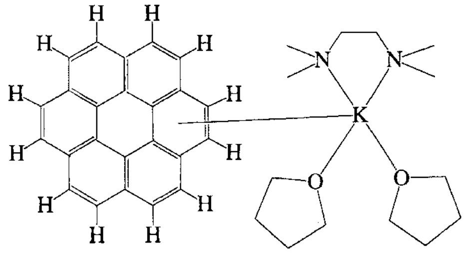
There is a growing interest in the nature of the interaction of π-delocalized carbanions with heavier alkali metal cations[1−4] as part of the long continuing interest in the structure of solvated ion pairs and alkali metal organic compounds[5−8].

In addition, we attempt to model the adsorption of potassium on a graphite surface[9] by interaction of potassium with extended molecular π systems, because the reactive properties of solid surfaces are often dramatically modified by adsorption of alkali metals[10], and it is a well-known phenomenon that potassium or alkali metals in general can catalyze a myriad of reactions of gaseous substances with surfaces[11]. This effect is exploited in a wide range of technological applications[12], and it has been observed that the oxidation rate of graphite can be greatly enhanced − by up to 10^4 times − by a predeposited potassium layer[13]. Little is, however, known on the nature of the graphite surface − potassium interaction (with or without additional adsorbate), such as adsorption site, distance above the surface, amount of charge transfer, corrugations generated on the surface, not to mention the mechanism of the alkali-catalyzed dioxygen-carbon reaction[9]. To help answer some of these questions and thereby substantiating assumptions made for theoretical studies involving potassium on graphite[9], we report here on the single crystal X-ray structure of bis(tetrahydrofuran)(tetramethylethylenediamine)potassium(1+)-coronene(1−) (**1**). To the best of our knowledge, **1** represents the first structural investigation of the coronene radical anion and also an organoalkali-metal complex with the largest aromatic π system[14].

The polycyclic aromatic hydrocarbon coronene (being ubiquitous on earth as a result of incomplete combustion of organic materials) and its radical anion are by themself also the subject of numerous studies[15]. Furthermore, coronene and other polyaromatics are often used as finite cluster models for the basal plane of graphite[16].

Results and Discussion

The molecular structure of one of the two independent molecules in the unit cell of **1** is shown in Figure 1. The other molecule differs only by the relative orientation of the solvent molecules with respect to the coronene moiety. A stereoscopic packing diagram of the unit cell is provided in Figure 2. Both molecules represent a monomeric solvated ion pair with the potassium ion showing the same unsymmetric π interaction with an external or outer ring of the coronene anion. Such a coordination mode has also been suggested for (coronene)(cyclopentadienyl)iron cations[18]. The K−C distances range from 318.5 to 345.5 pm in molecule 1 and 313.3 to 354.8 pm in molecule 2. A more or less symmetric η^6 coordination for potassium with wide K−C distance ranges is also found in a number of other compounds (see ref. in[1,2,4]).



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The coordination sphere around the potassium cations is completed by two THF and a chelating tmeda molecule. The structure is yet another example where tmeda effectively chelates a large potassium cation, contrary to common belief[4,6,8]. The monomeric character of the ion pairs is also remarkable as in most other potassium compounds with π perimeters polymeric chain structures are formed[4,7]. One might argue that with the solvate molecules, the structure discussed here does not represent a good model for the potassium-graphite surface interaction, yet, we would like to point out that the catalytic function of potassium most likely requires the interaction with both reactands: graphite *and* the gaseous adsorbate[9]. Since pure (solvent-free) organoalkali compounds are often very difficult to crystallize, we feel that **1** can very well be a model for a potassium-graphite interaction in the presence of

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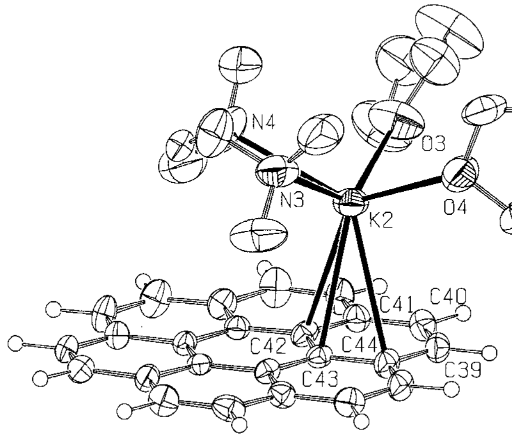

Figure 1. Molecular structure of **1** (two independent molecules in the unit cell, PLATON TME plot[17], 50% probability ellipsoids, hydrogen atoms of solvent molecules omitted for clarity). Selected distances [pm] and angles [°] (K−C/N/O distances for the other independent molecule are given in square brackets; "range" denotes the minimum and maximum for the C−C bond lengths of the same kind in the remaining coronene moiety): K2−C42 323.2(4) [324.6(4)], K2−C43 313.3(4) [318.5(4)], K2−C44 326.7(4) [325.4(4)], K2−C39 346.7(4) [338.9(4)], K2−C40 354.8(4) [345.5(4)], K2−C41 344.9(4) [340.9(4)] (only the three shorter contacts are drawn), K2 ring centroid 304.0(2) [300.9(2)], normal (K2 ring plane) 299.7(8) [299.0(20)], K2−O3 265.6(4) [268.8(4)], K2−O4 269.7(4) [266.1(4)], K2−N3 291.4(4) [285.9(4)], K2−N4 291.8(4) [284.1(4)]; O3−K−O4 88.1(1), N3−K2−N4 62.0(1), C39−C40 138.2(5) (range 136.6−138.0), C40−41/C39−C44 140.7(5)/141.4(4) (range 139.3−142.4), C41−C42/C43−C44 141.4(4)/143.2(4) (range 141.7−143.9), C42−C43 143.4(5) (range 141.5−142.7)

a gaseous adsorbate, especially in the absence of any better alkali-metal graphite-surface structural studies[9]. In this respect it is noteworthy that the nucleophilic solvent molecules do not displace the anion from the cation, but that some potassium-π interaction is retained. Solvation is estimated to increase the carbon-metal contact by approximately 20 pm[6]. It can be noted that neither the C−C bond lengths or angles in the ring closest to the potassium in **1** are significantly distorted (cf. caption to Figure 1) nor is there an overall distortion of the coronene anion when compared to the neutral molecule[19]. On an average the bond lengths are the same for the neutral and anionic system within experimental error, and the radical anion remains perfectly planar. This is in agreement with an open-shell UHF-PM3 calculation[20] on neutral and uninegative coronene. A plot of the electrostatic potential for coronene(1−) in Figure 3 points to a very flat energy surface for the metal cation above the delocalized anionic system in an electrostatically controlled interaction. Energy surfaces for metal cations above delocalized carbanions can be quite flat, the more so, the longer the cap-ring distance[6].

From the plot in Figure 3 it is also evident that the potassium does not coordinate to the centers of maximum charge density, which are mostly located at the C−H carbons. The unsymmetric binding above an outer hexagon can, however, be reproduced as a local minimum with a full geometry optimization on **1** (including solvate molecules[21]) based on the MNDO method for which potassium parameters were available[22]. Starting of the geometry optimization from different positions above an outer hexagon (above the different C atoms, the different C−C bonds or the ring center) led in nearly all cases to convergence in an unsymmetric position above the ring. From the calculations a potassium coordination above the inner hexagon is obtained as a slightly deeper minimum by about 8 kJ/mol. Regardless of the local site, the charge transfer from the potassium solvate moiety or even a bare potassium atom to coronene is calculated to be rather high and invariant (a numerical value of ca. 0.8 electrons is obtained which has, however, to be interpreted carefully[23] in view of the known deficiency of the Mulliken-population analysis in ionic systems).

Concerning the modelling of the potassium(with adsorbate)-graphite interaction, we can conclude that there is a slight preference for potassium being adsorbed (possibly somewhat asymmetrically) over a hexagon rather than a C−C bond or a C atom of the graphite plane. Furthermore, the potassium lies about 300 pm above the basal plane with no surface corrugations, and a rather high charge transfer from a potassium adsorbate to a graphite layer can be assumed.

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Experimental

[K(THF)$_2$(tmeda)][C$_{24}$H$_{12}$] (**1**): 0.44 g (1.47 mmol) of coronene and 0.12 g (2.94 mmol) of potassium metal in 10 ml of tmeda were treated for 1 h in an ultrasonic bath at 65°C to give a dark-green slurry. Addition of 17 ml of THF and 10 ml of diethyl

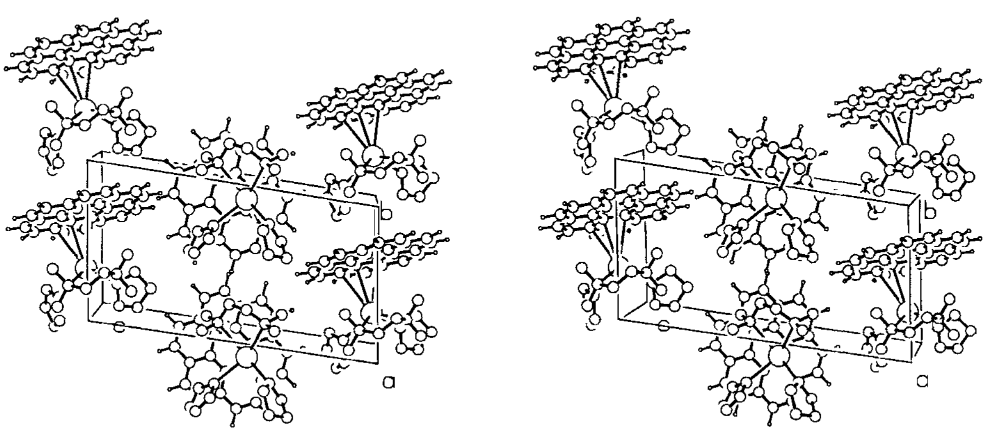

Figure 2. Stereo view of the unit cell of **1** (PLUTON plot[17])

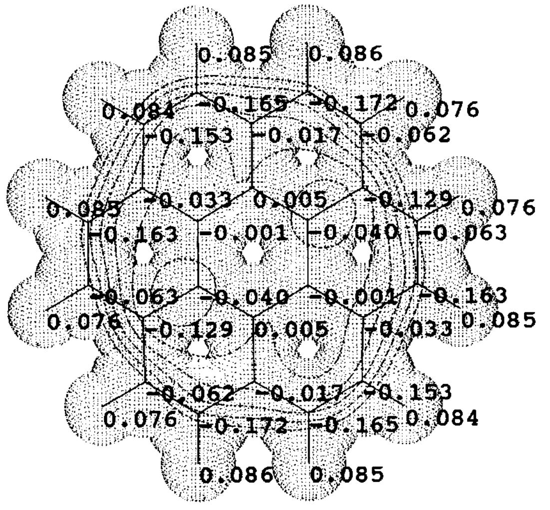

Figure 3. Charge distribution and electrostatic potential in the coronene radical anion according to an UHF-PM3 calculation[20]. Contour lines: −0.165 (minimum)/−0.160/−0.155/−0.150/−0.145/−0.140 (inside-out). The electrostatic potential is plotted 170 pm above the ring plane corresponding to the van der Waals surface (half thickness) of an aromatic system[24]

ether furnished a black-green solution from which highly air-sensitive black-green crystals could be grown at −26°C.

Crystal Structure Determination[25]: Empirical formula $C_{38}H_{44}KN_2O_2$, formula weight 599.88 g/mol, a = 934.6(3), b = 983.4(6), c = 1820.3(2) pm, α = 79.56(3), β = 78.44(2), γ = 85.76(4)°, Z = 2 (two independent molecules in the unit cell), d_{calc} = 1.237 g/cm^3, triclinic, $P1$, CAD4 Enraf-Nonius four-circle diffractometer, Mo-K_α radiation (λ = 71.069 pm, graphite monochromator), crystal size 0.10 × 0.20 × 0.15 mm^3, 165 K, ω-2Θ scan (4° $\leq$ 2Θ $\leq$ 50°), $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$, 12080 reflections measured, 10908 symmetry-independent, 8743 observed [$F > 6\sigma(F)$], μ(Mo-K_α) 2.0 cm^{-1}, linear decay correction (max. 1.110, min. 1.000; 18.9% decay in 163 hours), empirical absorption correction (DIFABS, max. 1.209, min. 0.945). Structure solution by direct methods (SHELXS-86)[26], both $P1$ and $P\bar{1}$ were tested for the structure solution and refinement. The statistics of the structural amplitudes point to an acentric space group and refinement was only successful in $P1$. In this acentric space group both enantiomers were tested for refinement, and the one with a significantly improved R value (12% vs. 20% before absorption correction) was fully refined. The atoms of the two independent molecules thus refined cannot be interchanged by a common center of inversion. Refinement: Bloc-matrix least-squares; non-hydrogen atoms were refined with anisotropic temperature factors (SHELX-76)[26]; hydrogen atoms fixed at idealized positions (C−H = 108 pm), 807 refined parameters, final R = 0.056, R_w = 0.058 ($R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, unit weights). Partial disorder and largest residual electron density (max. 0.455, min. −0.569 e Å^{-3}) in the coordinated solvent molecules.

Calculations and contour plots were performed with the program HyperChem (Version 3.0, Autodesk Inc., Sausolito, CA 94965, USA).

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