An Intercalation Compound of Graphite probably containing Potassium Cryptate Ions

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Potassium ions in KC_{36} can react with the 3-dimensional cryptand 'K222' (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) to yield a first-stage intercalation compound with an interlayer spacing d_i = 15.5 Å in which the K^+ ions are probably within the macroheterobicyclic cage.

Ternary compounds of graphite have been formed by allowing heterocyclic molecules such as hexamethylphosphoramide or tetrahydrofuran (THF) to react with a pure binary compound such as KC_{24}.[1] The enhanced stability which they all show is probably due to the decrease in reactivity of the ion brought about by the solvation-like co-ordination.[2] In spite of the fact that the complex formed between K^+ and the cryptand 'K222' (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) would not intercalate into graphite from various solutions,[3] it seemed reasonable to assume that, in view of the high affinity of the cryptand for K^+, intercalation of the macroheterobicyclic molecule could be achieved by allowing it to react directly with any K^+ ions present in the binary compound and formed *via* equilibrium (1) where G stands for

$$G + K \rightleftharpoons G^- + K^+ \qquad (1)$$

a plane of graphitic C atoms.

First attempts with KC_{24} immersed in a solution of K222 in THF resulted in the immediate formation of the well-known $KC_{24}(THF)_{2.3}$,[2] probably owing to the much larger rate of diffusion of the smaller THF molecules between the planes as compared with that of the cryptand. Further attempts were made under various conditions but all led to the conclusion that the best chance of obtaining a single phase would be to start with a binary compound with a potassium content just sufficient to permit the formation of a compact layer of the cryptate. The geometry of both K222 and the $[K^+(K222)]$ complex are known[4] and a rough estimate of the projected area of the latter showed it to correspond to *ca.* 80—100 Å^2, *i.e.*, the area of 30—40 graphite C atoms. Since a ***first-stage*** ternary compound results from a *second-stage* binary compound[5] (owing to the fact that the metal atoms or ions are redistributed over all the available surface of the plane), the third-stage binary compound KC_{36}, with a C/K ratio within the range of the values calculated, was chosen. This was allowed to react with the cryptand dissolved in a neutral non-polar solvent, to give a matt-black compound with a diffraction pattern characteristic of a single phase, first-stage ternary compound, with an interlayer spacing $d_I = 15.5$ Å. Although this value of d_I may seem inordinately high, similar values (14.9 Å) have been shown by ternary compounds of potassium in graphite containing dimethyl sulphoxide (DMSO).[6]

Although the reaction between KC_{36} and the cryptand was allowed to proceed for about 6 weeks, we were not certain that the reaction was complete; this could be one reason for the composition $K(K222)_{0.85}C_{36}$ which was found. If the reaction *was* complete, this would mean that the projected area of the $[K^+(K222)]$ complex is somewhat larger than was computed and would correspond to about 42 C atoms. Therefore in KC_{36} there would not be sufficient room to accommodate a sufficient quantity of the cryptand to form the complex with all the K^+ ions potentially available since, in the presence of K222, the equilibrium (1) can be expected to be shifted considerably to the right *via* reaction (2) which is probably irreversible.

$$K^+ + (K222) \rightarrow [K^+(K222)] \qquad (2)$$

The presence of K222 would thus force the ionization of the K atoms which were not already ionized. Any remaining non-complexed potassium atoms or ions could be accommodated easily in the cavities between the bulky quasi-spherical molecules of the complex, even if the latter were in a hexagonal close-packed array.

The presence of hydrogen in the solid was confirmed by broadline ^1H n.m.r.; from the width of the signal (11 G), it would appear that the intercalated cryptate is, as was expected, less mobile than in the free state, for which a signal of width 7 G was observed. Further confirmation of intercalation was provided by galvanostatic current *vs.* potential measurements performed during the electrolysis of a solution of KBF_4 in DMSO in the presence of K222 which showed a break at the ratio C (graphite)/K = 34.

The reaction between KC_{36} and the cryptand K222 does seem to give a first-stage ternary intercalation compound. Direct evidence confirming the presence of the K^+ ions *inside* the cage of the cryptand is lacking as yet but other possibilities seem most unlikely in view of the evidence available. If this hypothesis were to be confirmed, the novel combination of an extremely large interplanar distance (15.5 Å), a low concentration of donors (C/K > 34), and a well-shielded positive charge should yield some particularly interesting results.

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