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A comparative structural study of ternary graphite intercalation compounds containing alkali metals and linear or branched amines

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ABSTRACT

New donor-type ternary graphite intercalation compounds (GICs) containing alkali metals and branched amines are prepared by direct reaction of graphite with the alkali metal and amine. The new GICs include $M(iC3)_{0.4}C_{15-18}$ (M = Li, Na; iC3 = iso-propylamine; $d_i = 0.76$ nm) with a monolayer intercalate arrangement; and $Na(sC4)_{1.6}C_{18}$ (sC4 = sec-butylamine; $d_i = 1.34$ nm) and $Na(iC4)_{2.0}C_{28}$ (iC4 = iso-butylamine; $d_i = 1.28$ nm) with bilayer arrangements. Li-sC4-GIC and K-iC3-GIC are not formed using this reaction chemistry. M-iC3-GICs show galleries expanded by 0.06 nm more than that for $M(nC3)_{0.7-0.8}C_{16}$ (M = Li, Na; nC3 = *n*-propylamine). Unlike the case of rigid-sheet hosts where branched amines intercalate at a lower rate and with lower amine content, M-sC4-GICs and M-iC4-GICs readily form intercalate bilayers.

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1. Introduction

Alkylamines and alkylammonium ions are among the most widely studied guests employed in intercalation chemistry [1]. Intercalation compounds containing these species are applied as adsorbents for toxic compounds, photo and electrofunctional materials, and catalysts [2]. The insertion of large guests can generate microporosity within layered materials, and can contribute to the delamination of the layered hosts into individual sheets. The latter process, known as exfoliation, provides a route to reassembled materials with novel magnetic, optical and electronic properties [3]. Studies of the affect of intercalate geometry on reaction rate and product structure have provided a better understanding of this chemistry [1].

In donor-type graphite intercalation compounds (GICs), the graphene sheets are reduced and cations intercalate to maintain charge neutrality [4]. When the metal cation intercalate as solvated ions, ternary GICs are produced. Despite the long history of exploring GIC chemistry, the number of known GICs with amine intercalates or co-intercalates is surprisingly limited. The amine intercalates reported are ammonia or ammonium [5–7], methylamine [8], ethylenediamine [5], N,N,N',N'-tetramethylethylenediamine (TMEDA) [9], triethylamine [9], cryptand "K222" (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) [10], and 1,2-diaminopropane (12DAP) [11]. We recently added several new GICs to this list in reporting the synthesis of a homologous series of ternary GICs containing Na⁺ solvated by *n*-alkylamines with x carbon atoms, Na-nCx-GIC (x = 3, 4, 6, 8, 12, and 14) [12]. The smaller homologs (nC3 and nC4) intercalate with a parallel monolayer arrangement, whereas the larger homologs (nC8nC14) exhibit a parallel bilayer intercalate structure that is new to GICs. The intermediate length amine, nC6, can intercalate with either arrangement and can transition between the two.

In this report, we extend this work to study the intercalation of branched amines into graphite, and compare the resulting GIC structures and reaction chemistry of amines containing α or β substituents with their linear homologs.

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Fig. 1 – The amines studied and abbreviations (with normal boiling points).

Specifically, the new ternary GICs containing alkali metal cations Li, Na, or K and iso-propylamine (iC3), iso-butylamine (iC4), or *sec*-butylamine (sC4) are described and their reaction chemistries, structures, and compositions compared to GICs containing *n*-propylamine (nC3) and *n*-butylamine (nC4), Fig. 1. The results obtained help extend an understanding of the energetics of graphite intercalation, which should prove useful towards preparing GICs with large and complex galleries, and ultimately developing a rational synthesis of colloidal graphene dispersions.

2. Experimental

2.1. Synthesis

Reactions containing metallic Li were assembled in a Vac. Atm. PC-1 dry box under Ar (99.99+%). All other reagents and the obtained GICs were handled under N2 (Vac. Atm. He-43-2 box, <5 ppm H₂O and O₂). In a typical synthesis, 0.25 g of polycrystalline graphite powder (SP-1, Union Carbide, avg particle dia. 100 μ m) was mixed with 0.06 g of Na metal (99.95%, Alfa Aesar) (mol C/mol Na = 8) and the selected liquid amine (4 mL). Reactions using Li(m) and K(m) also used the same mole ratio of C/metal. Caution! Alkali metals are highly flammable when in contact with air and/or water and should be handled with care. The reaction mixtures were continuously stirred at ambient temperature under an inert atmosphere for 3 days (nC3, iC3 and nC4) or 7 days (sC4 and iC4). Caution! Pressure may increase and must be vented. The mixtures were then centrifuged and the liquid amine overlayer removed via syringe. GIC products were then dried in vacuo at 20 °C for 6 h. Some products were subjected to different drying times (2-72 h), as described in the text.

2.2. Characterization

Powder X-ray diffraction (PXRD) data (Rigaku MiniFlex II, Nifiltered Cu K α radiation) were collected for a total time of 15 min per run using 0.02° 2 θ steps, between 3° and 60° 2 θ . A plastic film seal was sufficient to prevent decomposition in air. This method provided sharp reflections without evidence of degradation for the much more reactive first-stage KC₈ at the same scan rate. PXRD (001) reflections were indexed according to the relation $I_c = d_i + (n - 1)(0.335 \text{ nm})$, where I_c is the unit cell repeat along the c-axis, d_i is the GIC gallery height, n is the GIC stage number, and 0.335 nm is the graphene sheet thickness. Thermogravimetric analyses (Shimadzu TGA-50) were performed under flowing Ar (20 mL/min) from RT to 800 °C at a heating rate of 5 °C/min. Elemental analyses for alkali metals were performed using Capillary Zone Electrophoresis (CZE). CZE analyses were performed on an HP^{3D}CE instrument equipped with a UV detector, using a 50 μm inner diameter, 56 cm long fused-silica capillary (47.5 cm to the detection window). The new capillary was sequentially conditioned by flushing with methanol (30 min), Milli-Q water (5 min), 1.0 M NaOH (30 min), Milli-Q water (5 min) and finally the background electrolyte (BGE) for 30 min. In between runs, the capillary was flushed with 0.1 M NaOH (2 min), Milli-Q water (3 min) and BGE (3 min). Separation was accomplished using an applied voltage of +15 kV. The capillary was thermostatted at 30 °C and solutions were injected hydrodynamically at 50 mbar for 5 s. Indirect detection was employed with the detection wavelength set at 210 nm. The background electrolyte used was 15 mM imidazole, pH adjusted to 5.2 with glacial acetic acid. GICs synthesized from different batches and separately analyzed showed amine contents agreeing within 2% and the alkali metal contents within 0.5%. The amine co-intercalate structures were optimized using the hybrid density functional method (B3LYP) with a 6-31+G(d,p) basis set and Gaussian 3.0 software.

3. Results and discussion

Except where noted, all the products obtained were first-stage GICs with intercalate galleries opened between all graphene sheets, i.e. no adjacent graphene sheets remain in the products. The first-stage compounds are all brilliant blue (see below).

3.1. Intercalation of iC3

The PXRD patterns obtained for the blue M-iC3-GICs (M = Li, $d_i = 0.760$ nm; M = Na, $d_i = 0.758$ nm) are shown in Fig. 2. The presence of Bragg reflections up to (004) indicates an ordered GIC arrangement along the c direction. A blue product was also obtained from the reaction with M = K, but displayed



Fig. 2 – The PXRD patterns of Na-iC3-GIC, Li-iC3-GIC, and Na-nC3-GIC. The *d* values (in nm) and assigned Miller indices are indicated for each reflection.



Fig. 3 – Schematic of intercalate orientations for Na-nC3-GIC, Na-iC3-GIC, Na-sC4-GIC, and Na-iC4-GIC. The inset shows the brilliant blue color of Na-sC4-GIC which is observed for all first-stage ternary GICs reported in this work. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

only a broad PXRD pattern (not shown), indicating a disordered structure. After subtracting the graphene sheet thickness of 0.335 nm, the expansion, Δd , related to intercalation of the M-iC3 complexes is ~0.43 nm. Because the Li and Na metal cation diameters (0.1–0.2 nm) are smaller than the minimum amine dimension, the cation contribution to gallery expansion is neglected (of course, the cations may indirectly be involved by affecting the orientation of the larger amine co-intercalates). For comparison, Fig. 2 also shows the PXRD pattern of the first stage Na-nC3-GIC (d_i = 0.701 nm, Δd = 0.37 nm), where the nC3 substituent lies parallel to the adjacent graphene sheets [12].

The increased gallery expansion by 0.06 nm for iC3 vs. nC3 co-intercalates conforms well with our calculated minimum dimensions (nC3 = 0.42 nm; iC3 = 0.49 nm) for these amines. To form these galleries, iC3 must therefore be oriented with either the C-C-C or N-C-C molecular axis parallel to the graphene sheets, leaving a -NH₂ or -CH₃ substituent, respectively, oriented towards the encasing graphene sheet. This branching is responsible for the increased gallery dimension relative to that of nC3, Fig. 3. PXRD data are not sufficient to locate alkali metal cation positions, which are shown schematically at the gallery centers. An analogous gallery height increase in ternary GICs for substituted organic cointercalates has been observed by Isaev et al. [13] in comparing K-benzene-GIC $(d_i = 0.895 \text{ nm})$ and K-1,2-dimethylbenzene-GIC $(d_i = 1.06 \text{ nm})$. The additional steric requirements for the branched amine may also affect the GIC compositions, as discussed in Section 3.4, resulting in a lower packing density of iC3 than nC3.

3.2. Intercalation of sC4

Fig. 4 shows the PXRD pattern of the blue product M-sC4-GIC (M = Na, $d_i = 1.341$ nm; M = K, $d_i = 1.335$ nm). The gallery expansion due to the M-sC4 complex is ~1.00 nm. K-sC4-GIC is similar to the Na analog, with slightly broadened peaks indicating decreased structural ordering along the c-axis. LisC4-GIC was not obtained under similar conditions – a black



Fig. 4 – The PXRD patterns of Na-sC4-GIC, K-sC4-GIC, and LinC4-GIC. The *d* values (in nm) and assigned Miller indices are indicated for each reflection.

product indicated only unreacted graphite (not shown). Comparing these PXRD patterns with that for Li-nC4-GIC [12] $(d_i = 0.704 \text{ nm}, \text{Fig. 4})$ shows the dramatic effect of the α -CH₃ substituent in sC4 on the resulting intercalate arrangement in the prepared GICs.

The large gallery height (1.34 nm) and high amine content (see Section 3.4) indicate a parallel bilayer structure for the sC4 co-intercalate, Fig. 3. Again, the limited number of diffraction peaks observed prevents cation position evaluation, and the alkali cations in the model are shown schematically. Considering the full gallery expansion, each monolayer dimension is \sim 0.50 nm, somewhat greater than that observed for the iC3 monolayers (0.43 nm). Other known donor types GICs with comparable gallery dimensions include Na-nC8-GIC $(d_i = 1.093 \text{ nm})$ [12], Li-DME-GIC (DME = dimethoxyethane, d_i = 1.162 nm) [14], and M-THF-GIC (M = Li, Na, K; THF = tetrahydrofuran, d_i = 1.245 nm) [15]. The parallel bilayer structure was reported for Na-nC8-GIC, whereas a T_d co-intercalate geometry about the metal cation was suggested in the other cases. In the current example, we believe that the bilayer structure is more likely.

3.3. Intercalation of iC4

Fig. 5 shows the PXRD patterns of M-iC4-GICs (M = Li, Na, K). For the blue Na-iC4-GIC product, the observed d_i = 1.28 nm and $\Delta d \sim 0.95$ nm are similar to those for sC4 described above. Based on the similar gallery dimensions and amine contents (see below), the intercalate galleries are also assigned a parallel bilayer structure similar to that shown in Fig. 3.

Li-iC4-GIC is obtained as a blue, but notable darker, product than the Na analog. The PXRD pattern indicates a predominantly stage 2 GIC ($I_c = 1.547$ nm, $d_i = 1.220$ nm) with a small amount of a stage 1 present ($d_i = 1.221$ nm). Increasing the reaction time to 2 weeks resulted in a poorly-ordered first-stage product ($d_i = 1.220$ nm, PXRD not shown). Passivation of the Li(m) surface with nitride (due to an N₂ impurity in the Ar atmosphere) could account for the higher stages obtained with Li(m). The broadened reflection at 0.314 nm is an overlap of the first-stage (004) (calculated position = 0.305 nm) and the second-stage (005)^{*} (calculated at 0.312 nm). A similar overlap occurs for the first-stage (003)



Fig. 5 – The PXRD patterns of Na-iC4-GIC, Li-iC4-GIC, and KiC4-GIC. The *d* values (in nm) and assigned Miller indices are indicated for each reflection. The starred assignments indicate a stage 2 GIC, others are for stage 1.

and second-stage (004)^{*} reflections, with the first-stage component on the low-angle side of the overlapping peak. A blue K-sC4-GIC ($d_i = 1.244$ nm) product can also be prepared, although the PXRD pattern indicates a poorly-ordered material that may also contain some stage 2 GIC. From the gallery dimensions and GIC compositions, all these M-iC4-GICs are assigned a parallel bilayer intercalate structure.

3.4. Compositional analyses

Table 1 provides a summary of the structural and compositional data of the GICs prepared in this work. The ternary GICs show two mass loss regions in TGA, Fig. 6. The first mass loss (RT to 200 °C) is ascribed to the volatilization of the amine intercalate; the higher temperature losses (>400 °C) to the decomposition of the graphite host structure. This high temperature mass loss is also observed for a graphite control sample, and is due to the presence of trace O₂ in the flow gas.

The amine content in M-iC3-GIC (10%) is much lower than that of the linear isomer intercalate M-nC3-GIC (15–19%), and also lower than that observed in other ternary GICs with organic cointercalates of similar molecular size such as K-TMEDA-GIC (14.4%) [9], Cs-n-pentane-GIC (14.6%) [16],



Fig. 6 – TGA mass loss curves for Na-iC3-GIC, Na-sC4-GIC, and Na-iC4-GIC.

Li-ethylenediamine-GIC (14.9%) [5], Cs-*n*-hexane-GIC (15.6%) [16], and Li-methylamine-GIC (17.4%) [5]. This lower packing fraction might relate to inefficient packing within the branched amine monolayer. A lower intercalate content due to the more rapid loss of the co-intercalate during drying (iC3 b.p. = $32 \,^{\circ}$ C; nC3 b.p. = $48 \,^{\circ}$ C) is unlikely and will be discussed below. There are other examples of decreased uptake of the iC3 amine isomer in intercalation reactions. For example, Cai et al. [17] reported that [Cd(1,5-naphthalenedisulfonate)(H₂O)₂] intercalates 4 moles of nC3, but only 3 moles of iC3. Similarly [Cd(μ_2 -N,O-p-NH_2C_6H_4SO_3)₂(H₂O)₂]_n intercalates 5 moles of nC3 but only 0.5 moles of iC3 [18].

The mass losses of the Na-sC4-GICs and Na-iC4-GICs are \sim 32%. These larger amine contents are consistent with the assigned bilayer structure, and are comparable to that for Na-nC8-GIC (29%) which was previously reported with a bilayer structure [12]. The lower amine contents observed for K-sC4-GIC and K-iC4-GIC (22–23%) might be related to their less ordered structures and some effect of packing with the larger cation.

The packing fraction, i.e. the volume of intercalates divided by the volume opened in the expanded galleries, are estimated in Table 1 from the known compositions, gallery dimension, the surface area per carbon atom in a graphene layer (0.0261 nm²), and using intercalate volume (in nm³):

Table 1 – Structural and compositional data of first-stage ternary M-amine-GICs.							
Amine	Cation M	d _i /nm	Intercalate arrangement	wt% M	wt% amine	Composition	Packing fraction
nC3 [*]	Li Na	0.700 0.701	Monolayer Monolayer	2.9 9.3	19.0 15.4	Li(nC3) _{0.8} C ₁₆ Na(nC3) _{0.7} C ₁₆	0.40 0.37
iC3	Li Na	0.760 0.758	Monolayer Monolayer	2.8 10.1	9.8 9.9	Li(iC3) _{0.4} C ₁₈ Na(iC3) _{0.4} C ₁₅	0.16 0.21
nC4	Li	0.704	Monolayer		14.8		
sC4	Na K	1.341 1.335	Bilayer Bilayer	6.6	32.9 21.7	Na(sC4) _{1.6} C ₁₈	0.31
iC4	Li Na K	1.221 1.280 1.244	Bilayer Bilayer Bilayer	4.3	32.0 23.4	Na(iC4) _{2.0} C ₂₈	0.27
n C3 compositional data from [12].							

Li⁺ (0.0016), Na⁺ (0.0060), C3 (0.0714) and C4 (0.0887) [19]. One notable result is that the monolayer arrangement with branched amines have much lower packing densities than the linear analogs (~0.2 vs. 0.4). The bilayer arrangements show an intermediate value (~0.3). The packing fractions of other ternary GICs show a wide range, from about 0.1 to 0.7. Examples include $K(NEt_3)_{0.43}C_{36}$ (NEt₃ = triethylamine) (0.08) [9], $K(TMEDA)_{0.7}C_{37}$ (0.2) [9], $K(CH_3NH_2)_3C_{24}$ (0.55) [8], and Li(CH₃NH₂)₂C₁₂ (0.68) [5].

When comparing these compositions and structures, it is important to consider the possible variation in composition, especially that of the amine co-intercalates, due to preparative conditions. Perhaps most significant is evacuation time; these GICs lose amine co-intercalate during evacuation. In order to evaluate these changes, mass losses of several Liamine-GICs were recorded as a function of evacuation time. Fig. 7 shows the normalized GIC mass as a function of evacuation time. Masses were normalized to the 2 h evacuated product (where no liquid phase co-exists) to avoid complications where excess liquid phase exists in the as-prepared sample. All samples show an approximately exponentially decreasing mass loss with time under vacuum. The rate of mass loss is lowest for Li-nC3-GIC and Li-nC4-GIC, and much greater for Li-iC4-GIC.

These loss rates do not correspond to the volatilities of the liquid amines (as indicated by their normal boiling points), and should result from different relative binding energies of amines in the GICs, or to the different co-intercalate diffusion rates for different gallery arrangements. The greater expansion in Li-iC4-GIC may facilitate more rapid diffusion of the intercalates out of the intercalate galleries. We are studying these effects and will report conclusions more fully elsewhere. However, the magnitude of mass losses observed provide a useful result. Our standard evacuation time in preparations of 6 h corresponds, at most, to mass loss change of <0.5%. The amine contents reported in Table 1 are therefore not variable with evacuation time above this extent, and the observations on packing fractions reported above remain valid despite different mass loss rates. Thus, we conclude that the lower amine content for iC3 (~10%) as compared to nC3 (16-19%) is associated with intercalate energetics or sterics rather than experimental conditions.



Fig. 7 – Normalized mass loss as a function of evacuation time. Lines are exponential fits to the data, with equations shown in the inset.

The intercalate mole ratios nC3/M are in the range of 0.7-0.8 whereas those for iC3/M are \sim 0.4. On the other hand, the branched C4 amine/M ratios are much larger, 1.6-2.0 (Table 1). These ratios are similar to others reported in the literature: 0.56 for Cs-n-butane-GIC [16], 0.7 for Na-nC3-GIC [12], 1.2 for Cs-acrylonitrile-GIC [20], 1.6–2.2 for M-NH₃-GICs (M = Li, Na, K, Rb, Cs) [21], and 2 for Li-methylamine-GIC [5]. For the Mamine-GICs reported in this work, the metal cations seem to play an only relatively minor role in determining GIC orientation or arrangement, in contrast to the M-12DAP-GIC series (M = Li, Na, K) we have reported previously [11]. On the other hand, the amine properties may be related to the formation of bilayer or monolayer intercalate structures. In this work, the amines with higher dipole moment, sC4 (1.28 D) and iC4 (1.27) formed bilayer GICs, whereas those with lower dipole moments formed monolayers - nC3 (1.17 D), iC3 (1.19), and nC4 (~1) [22].

3.5. Graphite vs. other hosts

Previous studies have reported on the affect of intercalate isomer type on reactivities or product structures for graphite or other hosts. Mizutani et al. [23] reported the synthesis of Li-1,2-diethoxyethane-GIC ($d_i = 1.12$ nm) vs. Li-1,2-dimethoxyethane-GIC ($d_i = 1.17$ nm). Neither the Li/ether ratio nor the orientation of the ether co-intercalates are reported. The same group [24] also reported the synthesis of a ternary M-tetrahydrofuran-GIC, whereas only the binary M-GICs were formed when 2-methyltetrahydrofuran or 2,5-dimethyltetrahydrofuran (M = alkali metal) were present. Similarly Isaev et al. [13] reported the ternarization study of KC₂₄ with aromatic compounds, where the ternary GICs were obtained with benzene and 1,2-dimethylbenzene, but not with 1,3-dimethylbenzene, 1,4-dimethylbenzene.

For other layered hosts, the presence of α -branched intercalates has been reported to retard or inhibit guest intercalation much more significantly than for β -, γ -, or no-branching. Examples include the intercalation of amines into Zn(O₃P- C_6H_5 ; H_2O [25], M^{II}(O₃PCH₃) (M = Co and Zn) [26], Cd(O₃PCH₃) [27], and $(V_x Nb_{1-x})OPO_4 \cdot yH_2O$ [28], as well as the intercalation of branched alcohols into VOPO₄ [29]. The intercalation of branched amines into rigid hosts such as metal phosphonates can be limited by the requirement that guests occupy specific sites on the host surface, resulting in what has been termed "selective intercalation". For example, Zn(O₃PC₆H₅). H₂O rapidly intercalates *n*-alkylamine, but require 1–3 weeks to form corresponding compounds with an α-branched amine [25]. Similarly, $M^{II}(O_3PCH_3)$ (M = Co and Zn) intercalates nC4 (no branching) and iC4 (β -branching), but not sC4 or tertbutylamine (α -branching) [26]; and Cd(O₃PCH₃) intercalates 2-methylbutylamine (β -branching) and 3-methylbutylamine $(\gamma$ -branching), but not 1-methylbutylamine (α -branching) [27].

However, as described above, GICs present a contrasting reaction chemistry for branched amines. The delocalized and somewhat variable charge on the graphene host, and perhaps the greater mechanical flexibility of graphene sheets, leads to the adoption of different intercalate arrangements for branched vs. linear guests, moreso than a selectivity for different intercalate species.

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