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The Intercalation of *N,N,N′,N′*-Tetramethyl-ethane-1,2-diamine (tmeda) into C_6Li and $C_{12}Li$

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Supporting Information

ABSTRACT: Liquid *N,N,N′,N′*-tetramethyl-ethane-1,2-diamine (tmeda) was intercalated into preprepared C_6Li or $C_{12}Li$. X-ray diffraction from the ternary compound indicates an identity period of 11.5 Å. The ^{13}C NMR line shifts show that tmeda molecules form a screen between the graphene planes and the lithium ions. Small-angle X-ray scattering showed that no higher structural ordering was present but revealed a progressive roughening of the surfaces with successive intercalation of lithium and amine into the graphite galleries.

Stage I C_8K readily absorbs hydrogen to a maximum hydrogen concentration of $x = 0.67$ in the C_8KH_x product at ambient pressure.[1] However, the phase instability of the hydrogenated lithium analogues presents significant challenges for rechargeable hydrogen storage.[2,3] As charge transfer from the alkali metal to graphite results in a strongly polarized electrostatic field that can have a significant effect on the interaction with adsorbed H_2 molecules,[4,5] our current aim is to affect the distribution of the donated electron within binary C_6Li and $C_{12}Li$ compounds with concomitant opening of the gallery structure. This is achieved by intercalating polar organic molecules, e.g., furans[6] and amines. Computational methods have shown that high hydrogen storage capacity is possible where the open gallery structures of layered materials are preserved, e.g., for Li-doped graphene oxide[7] or graphite pillared with $Li^+(THF)_x$ complexes.[8]

Amine intercalation into alkali graphite intercalation compounds has received renewed interest[9,10] because these graphitic materials are precursors for exfoliation into technologically important graphene. However, the Li−tmeda−graphite intercalation compound remains elusive when a direct, one-pot method is employed.[11] Here, we present the preparation of Li−tmeda−graphite ternary by gentle reflux of either binary stage I C_6Li or stage II $C_{12}Li$ with excess liquid tmeda. This particular intercalation compound was targeted with the view to study its hydrogen adsorption/desorption properties.

A solvent-less route was used to prepare C_6Li and $C_{12}Li$.[12] Liquid tmeda was subsequently intercalated into a binary compound. However, because the reaction was incomplete at room temperature, mixtures of the binary compound and tmeda were refluxed in an argon atmosphere. Figure 1 shows X-ray diffraction patterns displayed as I vs Q of C_6Li binary and Li−tmeda−graphite. Q is the scattering vector, $(4\pi \sin \theta)/\lambda$ and λ the wavelength, 1.54 Å. Pristine C_6Li displays the (001) reflection at 1.71 $Å^{-1}$ corresponding to an identity period of 3.7 Å, in good agreement with the literature value of 3.706 Å.[13] As the (001) reflection of the pristine C_6Li vanished after this treatment, complete conversion of the binary C_6Li into the ternary compound was achieved. The first three (00*l*) X-ray reflections of the ternary compound are numbered and correspond to an identity period of 11.5 Å, larger than that of the potassium−tmeda−graphite ternary, 8.94 Å, prepared by infiltrating $C_{36}K$ with tmeda.[14]

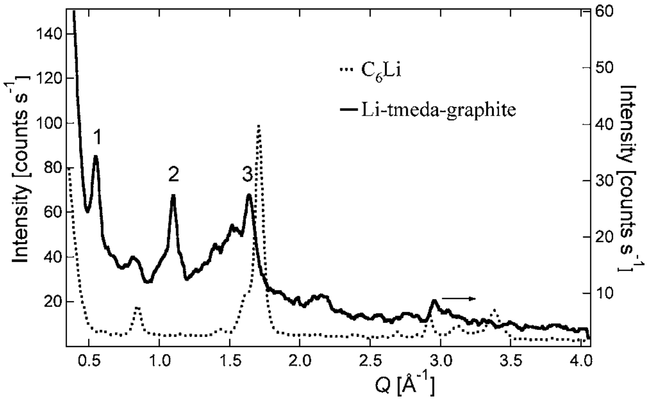

Figure 1. X-ray diffraction patterns displayed as I vs Q of C_6Li (dotted line) and $C_{12}Li$ after refluxing with tmeda (black line) showing the first three (00*l*) reflections for the 11.5 Å identity period. λ = 1.54 Å.

We note at this point that the (00*l*) reflections vanished after prolonged vacuum treatment, and a series of reflections corresponding to an identity period of 9.1 Å became more noticeable (Figure S1, Supporting Information). The dimensions of the gallery height after subtraction of the thickness of the graphite sheet, 3.35 Å, from the 11.5 Å and 9 Å identity periods are commensurate with the length and width of a tmeda molecule when considered as a short cylinder (Figure S2). This result suggests that a reorientation of the tmeda molecule from perpendicular to parallel with respect to the graphene planes had occurred after vacuum treatment. Using the gallery height, an estimate of the area of a tmeda molecule from the radius of the cylinder and the radius of the lithium ion, the volume occupied by the tmeda molecule was calculated according to

$$V_{\text{tmeda}} = \pi r_{\text{tmeda}}{}^2 \times (I_c - 3.35) - \frac{4\pi r_{\text{Li}}{}^3}{3}$$

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The volume of 146 Å^3 is in rough agreement with the volume estimated by MM2 energy minimization methods, 133 Å^3.[15]

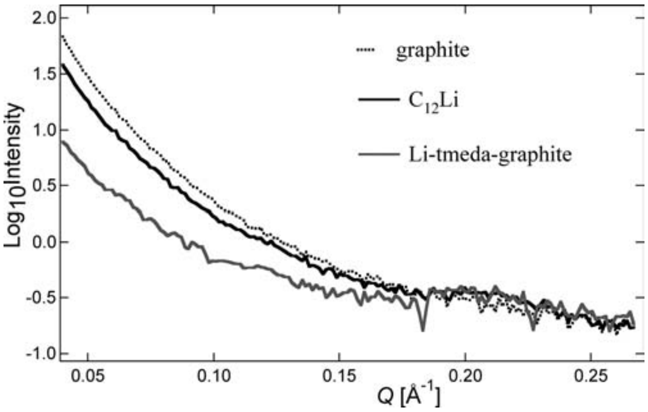

Figure 2. Small angle X-ray scattering measurements displayed as $\log_{10} I$ vs Q of Ceylon graphite (dotted line), $C_{12}Li$ (black line), and $C_{12}Li$ after refluxing with tmeda (gray line). λ = 1.54 Å.

The SAXS pattern of the ternary compound prepared using $C_{12}Li$ as the precursor is shown in Figure 2 together with that obtained from graphite and $C_{12}Li$. Scattering from $C_{12}Li$ shows a weak maximum centered at 0.21 Å^{-1}. Previously, we reported that the small angle scattering from binary C_6Li and $C_{12}Li$ and the tetrahydrofuran ternary originates from lateral inhomogeneities that result from the distribution of lithium in the galleries rather than the presence of higher stage intercalation compounds.[6] An indication of the nature of the surfaces was obtained from the slope of the log *I* vs log *Q* plots (Figure S3): graphite, −3.7; $C_{12}Li$, −3.4; and Li−tmeda−graphite, −2.6, suggesting a progressive roughening of the surface with successive intercalation of lithium and amine. The ternary compound having the same identity period was formed when either C_6Li or $C_{12}Li$ was used as the precursor material. This result supports the Staging Domain or Pleated Layer model proposed by Daumas and Hérold. According to this model, the intercalant in an *n*-stage compound covers a fraction of 1/*n* of the area of each graphene sheet, rather than the intercalant being present only in one of every *n* sheets.[16] The experimental tmeda/Li ratio of 1:1 was obtained from the Li, C, H, and N content. A stylized image of the Li−tmeda−graphite ternary is presented in the Supporting Information, Figure S4.

The ^{13}C NMR spectra of graphite, C_6Li, and the ternary compound are shown in Figure 3. These spectra arise from the combined effects of the diamagnetic chemical shift and the paramagnetic Knight shift[17] in these semimetals. The shifts are anisotropic, displaying a downfield peak resulting from $\delta_{a,b}$ absorption and an upfield peak from δ_c absorption due to particles with their *c* axis parallel to the field, as demonstrated for K−benzene−graphite ternaries.[18,19] For C_6Li and the Li−tmeda−graphite ternary compound, the δ_c absorption peaks occur at +80 ppm and +50 ppm, respectively. We note here that our graphite reference in ∼12T field shows absorption at −20 ppm, slightly lower than the −50 ppm shift observed in a 2T[20] or 6T[21] field. However, the shift for C_6Li of 100 ppm is in reasonable agreement with the literature value of 106 ppm.[20] The result of the intercalation of the tmeda into the binary compound is a shift of the δ_c peak to higher field, indicating that the graphene and Li layers have been decoupled; i.e., the tmeda molecules form a screen. A previous study of M−THF−graphites (M = K, Rb, Cs) has shown that charge donated by the alkali metal is distributed between the graphene planes and the furan.[22] The ^{13}C NMR spectrum of liquid tmeda is shown in Figure 3 as a control.

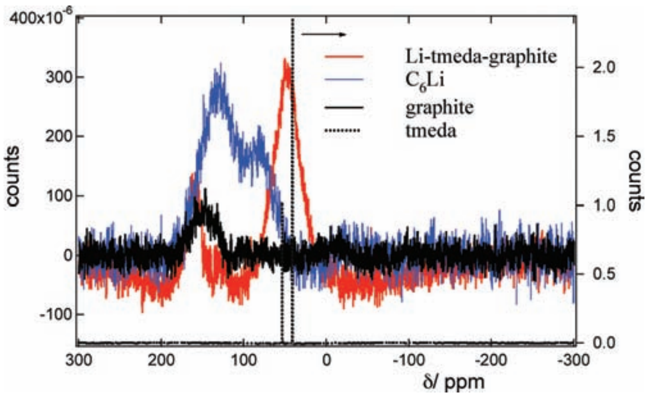

Figure 3. ^{13}C NMR spectra of Ceylon graphite (black line), C_6Li (blue line), Li−tmeda−graphite ternary (red line), and tmeda (dotted line).

We have shown that it is possible for Li to attract tmeda into the sterically challenged environment of preprepared lithium intercalated graphite galleries of 3.7 Å spacing. On the other hand, the direct combination of Li, tmeda, and graphite failed to produce the ternary compound.[11] For the latter case, prior coordination of tmeda to lithium must inhibit the entry of the ligand−metal ensemble into the small graphitic interlayer distances. Our attempts to form a Li−H−graphite ternary by the direct combination of Li, H_2, and graphite in the reactor at 200 °C and 450−600 rpm agitation not only failed but this approach also inhibited the formation of the C_6Li and $C_{12}Li$ binaries that are readily formed in an argon atmosphere. The lack of intercalation can be reconciled in terms of the enthalpy of formation of the alkali metal hydrides: higher in the case for LiH, −44 kcal mol^{-1}, than for KH, −14.11 kcal mol^{-1}.[23] Returning to tmeda, the one-pot synthesis failed to produce the ternary compound not because of a lack of an association of this ligand for lithium but because of this association. We found that the related Lewis base ethylenediamine (en) was able to form a graphite intercalation compound when $C_{12}Li$ was mixed with this liquid amine at room temperature in a capillary, Figure S5. However, the synthesis was poorly reproducible when attempted at gram-scale, most likely a result of H_2 evolution and lithium deintercalation. The deep blue filtrate from the reaction displayed an absorption maximum at 589 nm, indicating the formation of the amide $H_2NCH_2CH_2NH^- Li^+$.[24] Li−en−graphite has been reported.[11,25]

Despite the controversy over the mechanism of tmeda-activated lithium,[26] tmeda is still widely used as a ligand for organolithium reagents, notably $\mathrm{Bu^nLi}$, to increase its reactivity toward metalation. Though the crystallography presented here cannot provide an insight into the thermodynamic or kinetic aspects of the activation, in practice the moderately air-sensitive Li−tmeda−graphite could find use as a convenient metalation reagent because the solid byproduct, graphite, can be readily separated from the soluble products.

Our study of the in-plane structure of the ternary compound using exfoliated sheet graphite (Papyex) containing partially oriented graphitic crystallites will be presented in a future publication.

N,*N*,*N*′,*N*′-tetramethyl-ethane-1,2-diamine was intercalated into either stage I C_6Li or stage II $C_{12}Li$ to form a new coordination compound having an identity period of 11.5 Å. The use of the binary precursors allows the preparation of this ternary compound not accessible by the one-pot method.[11]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, analyses, X-ray diffraction, X-ray scattering patterns, and graphics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Beaufils, J. P.; Trewern, T.; Thomas, R. K.; White, J. W. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2387−2397. (b) Trewern, T.; Thomas, R. K.; Naylor, G.; White, J. W. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2369−2385. (c) Trewern, T.; Thomas, R. K.; White, J. W. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2399−2410.

(2) Miyaoka, H.; Ishida, W.; Ichikawa, T.; Kojima, Y. *J. Alloys Compd.* **2011**, *509*, 719−723.

(3) Srinivas, G.; Lovell, A.; Howard, C. A.; Skipper, N. T.; Ellerby, M.; Bennington, S. M. *Synth. Met.* **2010**, *160*, 1631−1635.

(4) Stead, W. J.; Jackson, I. P.; Mccaffrey, J.; White, J. W. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1669−1682.

(5) Wielopolski, P. A.; White, J. W. *Mol. Phys.* **1990**, *69*, 959−972.

(6) Henderson, M. J.; White, J. W. *Int. J. Energy Eng.* **2011**, *1*, 19−26.

(7) Tylianakis, E.; Psofogiannakis, G. M.; Froudakis, G. E. *J. Phys. Chem. Lett.* **2010**, *1*, 2459−2464.

(8) Han, S. S.; Jang, S. S. *Chem. Commun.* **2009**, 5427−5429.

(9) Lerner, M. M.; Maluangnont, T.; Gotoh, K.; Fujiwara, K. *Carbon* **2011**, *49*, 1040−1042.

(10) Maluangnont, T.; Sirisaksoontorn, W.; Lerner, M. M. *Carbon* **2012**, *50*, 597−602.

(11) Maluangnont, T.; Lerner, M. M.; Gotoh, K. *Inorg. Chem.* **2011**, *50*, 11676−11682.

(12) Postnikov, V. A.; Kakuliya, T. V.; Khananashvili, L. M.; Isaev, Y. V.; Novikov, Y. N.; Volpin, M. E. *Russ. Chem. Bull.* **1979**, *28*, 626−627.

(13) Sangster, J. *J. Phase Equilib. Diffus.* **2007**, *28*, 561−570.

(14) Merle, G.; Letoffe, J. M.; Rashkov, I. B.; Claudy, P. *J. Therm. Anal.* **1978**, *13*, 293−305.

(15) Aathimanikandan, S. V.; Sandanaraj, B. S.; Arges, C. G.; Bardeen, C. J.; Thayumanavan, S. *Org. Lett.* **2005**, *7*, 2809−2812.

(16) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **2002**, *51*, 1−186.

(17) Slichter, C. P. *Principles of Magnetic Resonance*; Harper & Row: New York, 1963.

(18) Quinton, M. F.; Legrand, A. P.; Facchini, L.; Beguin, F. *Synth. Met.* **1988**, *23*, 271−276.

(19) Beguin, F.; Setton, R.; Facchini, L. *Synth. Met.* **1983**, *7*, 263−269.

(20) Conard, J.; Estrade, H.; Lauginie, P.; Fuzellier, H.; Furdin, G.; Vasse, R. *Physica B* **1980**, *99*, 521−524.

(21) Conard, J.; Gutierrezlebrun, M.; Lauginie, P.; Estradeszwarckopf, H.; Hermann, G. *Synth. Met.* **1980**, *2*, 227−236.

(22) Jegoudez, J.; Mazieres, C.; Setton, R. *Carbon* **1986**, *24*, 747−756.

(23) Elansari, L.; Marassi, R.; Tossici, R.; Gachon, J. C.; Antoine, L.; Nalimova, V. A.; Guerard, D. *Mol. Cryst. Liq. Cryst.* **1998**, *310*, 309−314.

(24) Reggel, L.; Friedel, R. A.; Wender, I. *J. Org. Chem.* **1957**, *22*, 891−895.

(25) Rudorff, W. *Chimia* **1965***19*, 489−499.

(26) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448−454.