Acetylide Chemistry

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Evidence of Solubility of the Acetylide Ion C_2^{2-}: Syntheses and Crystal Structures of $K_2C_2{\cdot}2\,NH_3$, $Rb_2C_2{\cdot}2\,NH_3$, and $Cs_2C_2{\cdot}7\,NH_3$

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Most alkali- and alkaline-earth-metal acetylides of composition $A^{I}_2C_2$ (A^I = Li–Cs) and $(AE)^{II}C_2$ ($(AE)^{II}$ = Mg–Ba) have been known since the 19th century.[1,2] Very early crystal structure investigations had already revealed that they contain C_2^{2-} dumbbells,[3,4] but the complex phase behavior of these compounds was elucidated only very recently.[5] In the first half of the last century, CaC_2 in particular, which is accessible from CaO and coal, attracted a lot of interest as an industrial feedstock of acetylene by hydrolysis.[6] Owing to the limited petroleum resources, this reaction has found a revival within the last years.[7] Apart from hydrolysis however, reports on further reactions of alkali- and alkaline-earth-metal acetylides are quite rare, which is surely due in part to the fact that these compounds are insoluble in common solvents.[8] However, during the synthesis of ternary copper acetylides A^ICuC_2 with A^I = K–Cs, we observed that a suspension of $A^{I}_2C_2$ in liquid ammonia reacts with CuI at temperatures as low as −78 °C within minutes.[9] To clarify whether this reaction can be interpreted as a (low) solubility of $A^{I}_2C_2$ in liquid ammonia, we decided to investigate the system $A^{I}_2C_2/NH_3(l)$ in more detail. The versatility of liquid ammonia to stabilize unusual main-group-element clusters has been shown by several impressive examples.[10] Herein we report the crystal structures of the ammoniates $K_2C_2{\cdot}2\,NH_3$ (**1**), $Rb_2C_2{\cdot}2\,NH_3$ (**2**), and $Cs_2C_2{\cdot}7\,NH_3$ (**3**),[11a–c] which are the first examples of binary acetylide solvates. Additionally, the crystal structure of $[Li(NH_3)_4]C_2H$ (**4**),[11d] which contains the hydrogen acetylide anion C_2H^-, is briefly presented.

Single crystals of **1**–**4** crystallized from suspensions of $A^{I}_2C_2$ (A^I = Li, K–Cs) in liquid ammonia at temperatures below −40 °C (see the Experimental Section). The observation that compounds containing C_2^{2-} or C_2H^- anions are obtained under very similar synthetic conditions points to the fact that the equilibrium between C_2^{2-} and C_2H^- in liquid ammonia is very much dependent upon the specific synthetic conditions, such as the corresponding cation, temperature, or solubility versus precipitation/crystallization. This has already been reported for the equilibrium between LiC_2H and Li_2C_2, as upon evaporation of ammonia the LiC_2H formed initially transforms into Li_2C_2.[24] LiC_2H can only be stabilized by addition of a donor ligand, such as ethylenediamine.[25]

Compounds **1**–**3** crystallize in the monoclinic space groups $P2_1/n$ and $C2/m$. They exhibit significant differences concerning the coordination spheres of the respective C_2^{2-} dumbbells as well as the linkage patterns of the structural units, which build up the particular crystal structures. The observed C–C bond lengths (listed in Table 1) are slightly elongated compared to the expected value for a C–C triple bond as obtained from previous experimental data (acetylene 1.205 Å,[12] K_2C_2 1.19(1) Å,[5b] CaC_2 1.191 Å[13]). This divergence is surprising at first sight, but in several theoretical investigations, C–C distances ranging from 1.254 Å to 1.264 Å were calculated for Rb_2C_2,[14] Cs_2C_2,[14] and CaC_2.[15] It should be further noted that most experimental data were obtained from measurements recorded at ambient conditions. Thus, a dynamic disorder of the C_2^{2-} dumbbells around their center of gravity is likely,[16] which would reduce the C–C distances determined by diffraction. Accordingly, the "real" C–C distance within an alkali- or alkaline-earth-metal acetylide is somewhat ambiguous. Interestingly, in a neutron diffraction experiment on BaC_2 at 20 K we obtained a C–C distance of 1.243(3) Å, but the quality of the data and the resulting refinement was only modest.[5g]

Table 1: Space groups and selected interatomic distances for $K_2C_2{\cdot}2\,NH_3$, $Rb_2C_2{\cdot}2\,NH_3$, and $Cs_2C_2{\cdot}7\,NH_3$.

Compound	C–C [Å]	C-A^I [Å] (A^I = K–Cs)	C···H [Å]	Space group
$K_2C_2{\cdot}2\,NH_3$	1.241(3)	2.994(2)–3.339(2)	2.34(2), 2.53(3)	$P2_1/n$
$Rb_2C_2{\cdot}2\,NH_3$	1.238(12), 1.238(11)	3.248(3)–3.460(4)	2.31(5)–2.44(8)	$C2/m$
$Cs_2C_2{\cdot}7\,NH_3$	1.21(2)	3.444(5)–3.538(6)	2.30(8)–2.48(4)	$C2/m$

Herein we present the results of low-temperature investigations (T = 123(2) K), so that the dynamic disorder of the C_2 dumbbells can be assumed to be almost frozen. Similar slightly enhanced C–C distances were obtained by other authors on acetylides of composition $(AE)^{II}(C{\equiv}CR)_2$ with $(AE)^{II}$ = Ca–Ba and R = organic substituent.[17] Other structure-dependent effects, which might also affect the (different) C–C distances within **1**–**3**, will be discussed below.

The anion in $K_2C_2{\cdot}2\,NH_3$ (**1**) is coordinated by six potassium cations, leading to a heavily distorted octahedral environment (coordination number CN = 6; see Figure 1 a). In contrast, the two acetylide ions in $Rb_2C_2{\cdot}2\,NH_3$ (**2**)

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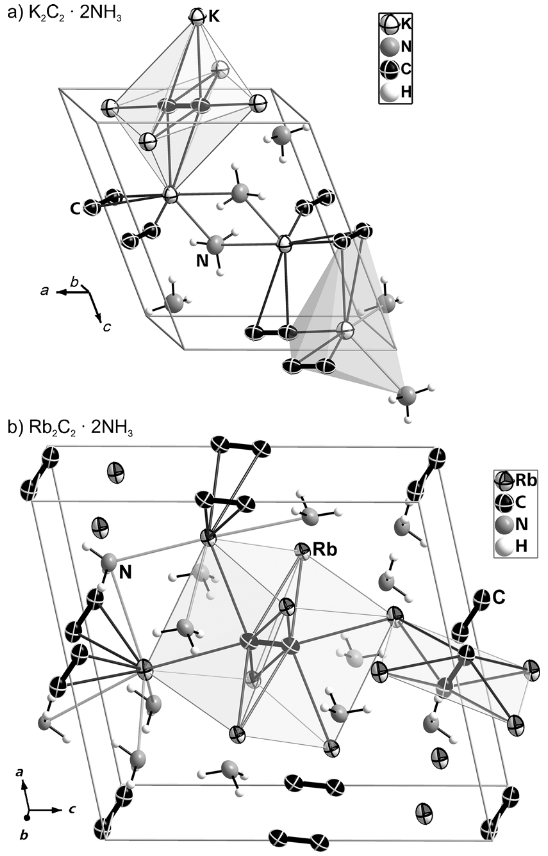


Figure 1. a) Crystal structure of $K_2C_2{\cdot}2NH_3$. The distorted octahedral coordination sphere around one C_2^{2-} dumbbell is shaded. The coordination sphere around one K^+ cation is also emphasized. b) Crystal structure of $Rb_2C_2{\cdot}2NH_3$ with a square-prismatic and a square-planar Rb coordination around two C_2^{2-} dumbbells, respectively. Ellipsoids are set at 70% probability.

(Figure 1b), which are in each case generated by one crystallographically independent carbon atom, are surrounded by eight and four rubidium cations respectively, yielding a slightly distorted cubic (CN = 8) and a square-planar coordination sphere (CN = 4). In a similar manner, the C_2^{2-} dumbbell in the asymmetric unit of $Cs_2C_2{\cdot}7NH_3$ (**3**) is located in a square-planar Cs coordination sphere (CN = 4). These coordination spheres are completed by contacts to NH_3 molecules. The C–A^I distances in **1**–**3** (Table 1) are in good agreement with the corresponding distances in the binary acetylides K_2C_2 (3.009(5)–3.146(3) Å),[5b] Rb_2C_2 (3.107(4)–3.447(6) Å),[5d] Cs_2C_2 (3.21(3)–3.65(2) Å),[5d] and in the hydrogen acetylide ammoniates $K_2Zn(C_2H)_4{\cdot}2NH_3$ (2.997(3)–3.291(3) Å) and $K_2Cd(C_2H)_4{\cdot}2NH_3$ (3.023(3)–3.375(4) Å).[18]

It is not entirely surprising that the C···H distances between C_2^{2-} and NH_3 (Table 1) in each of the three presented compounds are significantly shorter than the sum of the van der Waals radii,[19] so that moderate to weak hydrogen bonds have to be taken into account. Consequently, the coordination spheres of the C_2^{2-} ions can be enlarged to $(C_2)K_6(NH_3)_4$ (CN = 6 + 4), $(C_2)Rb_8(NH_3)_4/(C_2)Rb_4(NH_3)_8$ (CN = 8 + 4/4 + 8), and $(C_2)Cs_4(NH_3)_8$ (CN = 4 + 8). These C···H–N hydrogen bonds might also be responsible for the slightly elongated C–C distances within the C_2 dumbbells, as they remove electron density from the anions. Additionally, the C–C bond lengths of **1**–**3** slightly decrease from 1.241(3) Å for the potassium to 1.21(2) Å for the cesium compound. But in the case of $Cs_2C_2{\cdot}7NH_3$ (**3**), slightly enlarged anisotropic displacement parameters of the carbon atoms are found, pointing to a librational disorder, which should reduce the apparent C–C distance.

The linkage of the $(C_2)A^I_n$ polyhedra ($n = 4$, 6, 8) described above and the associated formation of the ammonia-containing crystal structures are quite different for **1**–**3**. As shown in Figure 2a, $K_2C_2{\cdot}2NH_3$ (**1**) consists of C_2^{2-}-centered K_6 octahedra, which are edge-linked to form layers being separated by ammonia molecules. This two-dimen-

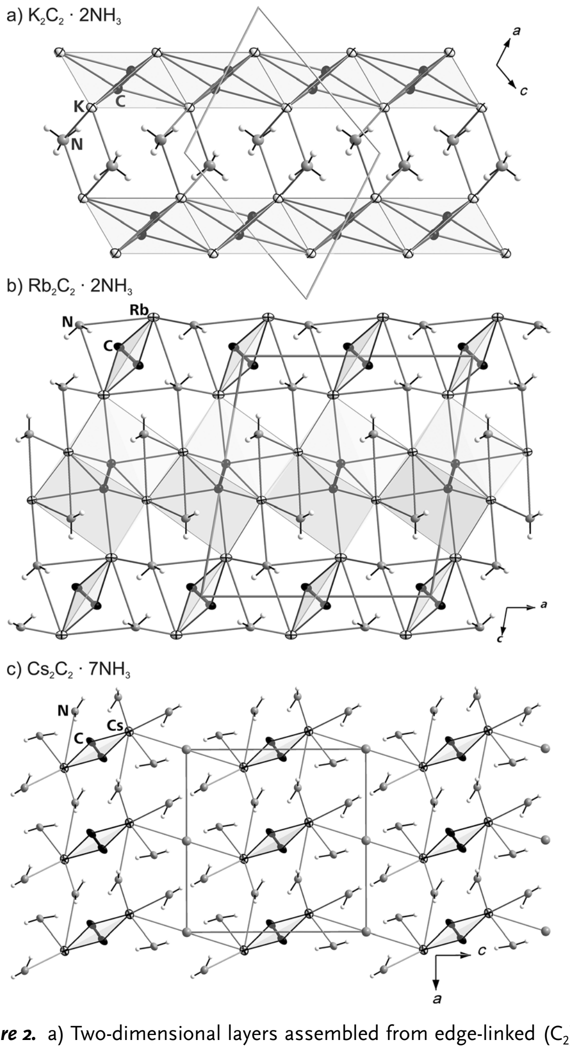


Figure 2. a) Two-dimensional layers assembled from edge-linked $(C_2)K_6$ octahedra (emphasized in gray) in $K_2C_2{\cdot}2NH_3$ (**1**). These layers are separated by ammonia molecules. b) $Rb_2C_2{\cdot}2NH_3$ (**2**): three-dimensional network built up from layers of edge-linked $(C_2)Rb_8$ cubes connected by vertices with strands of planar edge-linked $(C_2)Rb_4$ units (shaded parts of the picture) to form channels filled with NH_3 molecules. c) One-dimensional strands of edge-linked planar $(C_2)Cs_4$ units running parallel to the *b* axis in the ammonia-rich $Cs_2C_2{\cdot}7NH_3$ (**3**). These strands are completely separated from each other by NH_3 molecules. In (c) the isotropically refined N4 atom is shown without its H atoms. Ellipsoids are set at 50% probability.

sional part of **1** can be understood as a distorted variant of the layers in the CdI_2 type structure (see the Supporting Information, Figure S1).

In contrast, $Rb_2C_2{\cdot}2NH_3$ (**2**) forms a three-dimensional network built from layers of $(C_2)Rb_8$ cubes linked among each other by six of their eight vertices. The remaining two vertices of each cube are further connected with strands of almost planar $(C_2)Rb_4$ units, which are linked by common edges among each other (Figure 2b). The resulting channels are filled with NH_3 molecules (Supporting Information, Figure S2). The characteristic structural motifs of the ammonia-rich compound $Cs_2C_2{\cdot}7NH_3$ (**3**) are one-dimensionally extended, completely isolated strands of edge-linked $(C_2)Cs_4$ units that are surrounded by ammonia (Figure 2c). It is evident that, particularly with regard to the isostructural binary acetylides Rb_2C_2 and Cs_2C_2,[5d] the acetylide ammoniates of these alkali-metal cations display a wide structural variability, which is a consequence of a varying ammonia content as well as the role of ammonia as a cation-coordinating dipole and a hydrogen-bond donor.

The solubility of acetylene in liquid ammonia solution is well-investigated.[20] The addition of alkali metals to this solution leads to solvated hydrogenacetylide ions C_2H^-.[1a–d] However, prior to our work it seemed very unlikely that the C_2^{2-} ion can also be stable in any protic solvent because of its high charge and small size. Only few examples for similar highly charged anions in solution have been reported, for example Sn_4^{4-}, Pb_4^{4-},[21] and Sb_8^{8-}.[22] For these species liquid ammonia constitutes a well-suited medium owing to the fact that oxidation by protons is kinetically unfavorable.[23]

Thus, while the alkali-metal hydrogenacetylides A^IC_2H ($A^I = Na–Cs$) are routinely synthesized in liquid ammonia[1a–d] (see also the Experimental Section), the alkali metal acetylides $A^I_2C_2$ have only been accessible by high-temperature routes.[1a,b,5b,d,24] With the preparation of $K_2C_2{\cdot}2NH_3$, $Rb_2C_2{\cdot}2NH_3$, and $Cs_2C_2{\cdot}7NH_3$ from the corresponding binary acetylides in liquid ammonia, we now show that the C_2^{2-} anion is also solvated in NH_3 in sufficient quantities to form crystals of **1**–**3**.

Furthermore, the following conclusion can be drawn from these observations: in liquid ammonia, the acetylene molecule C_2H_2 ($pK_S \approx 25$), the hydrogenacetylide ion C_2H^-, and the acetylide ion C_2^{2-} most likely exist in equilibrium. This assumption is strongly supported by the fact that it was possible to obtain the novel hydrogen acetylide compound $[Li(NH_3)_4]C_2H$ (**4**) by dissolution and protonation of Li_2C_2. As mentioned earlier, LiC_2H transforms to Li_2C_2 upon evaporation of ammonia.[24] Here, at lower temperatures the ammoniate of LiC_2H is crystallized, which strongly corroborates the proposed equilibrium between C_2^{2-} and C_2H^-. Furthermore, the crystal structure of **4** contains the first example of a C_2H^- anion without any metal contacts (Figure 3). Scheme 1 illustrates the proposed equilibrium between C_2H_2, C_2H^-, and C_2^{2-}. The equilibrium lies mainly on the side of C_2H^-, as upon evaporation of the solvent A^IC_2H precipitates for $A^I = Na–Cs$, so that the equilibrium is shifted even more to the side of C_2H^-. For $A^I = Li$ however, the opposite behavior is found, as upon evaporation of ammonia Li_2C_2 is formed and at lower temperatures $[Li(NH_3)_4]C_2H$ (**4**) crystallizes. At −40 °C, however, the obviously lower solubility of the acetylide ammoniates **1**–**3** prevails, thus leading to the crystallization of these compounds.

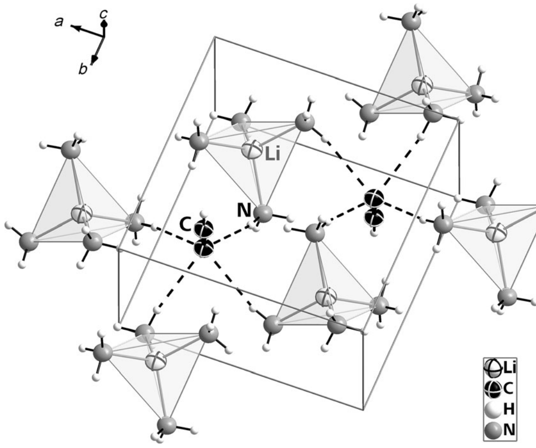
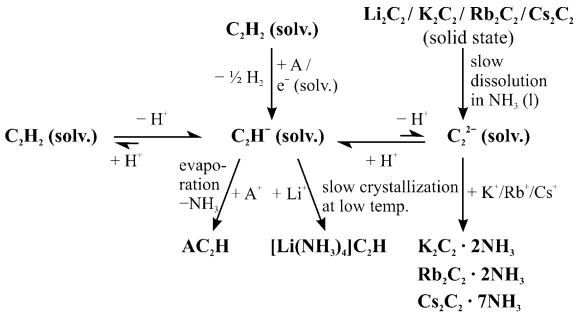


Figure 3. Crystal structure of $[Li(NH_3)_4]C_2H$ (**4**). The formally negatively charged carbon atom builds up square-pyramidally aligned hydrogen bonds with the $[Li(NH_3)_4]^+$ complexes. The H atom of the C_2H^- anion isolates the two-dimensional layers which run along the (001) plane against each other. Ellipsoids are set at 50% probability.



Scheme 1. Postulated equilibrium of the three solvated species C_2H_2, C_2H^-, and C_2^{2-} in liquid ammonia. Either a stoichiometric amount of alkali metal is added to an ammonia–acetylene solution, resulting initially in C_2H^-, or binary acetylides $A^I_2C_2$ (with $A^I = Li$, K–Cs) are dissolved in NH_3(l), initially resulting in C_2^{2-}. Evaporation of the solvent leads to the precipitation of the alkali-metal hydrogen acetylides A^IC_2H ($A^I = Na–Cs$) or Li_2C_2. At low temperatures, the slow crystallization of **1**–**4** is observed.

Therefore, it seems conceivable that under certain conditions, alkali-metal acetylides or even alkaline-earth-metal acetylides can be prepared from solution. This is an important step towards the preparation of new carbides from solution. Furthermore, it opens the door for a novel acetylide chemistry in solution.

In summary, we have been able to synthesize the first solvates of binary acetylides ($A^I = K–Cs$) and characterize them by single-crystal X-ray diffraction. To our knowledge, they further constitute the only examples of single-crystal studies of binary alkali-metal acetylides at all. But most importantly, they give the first evidence of a solubility of the C_2^{2-} anion in any solvent. Li_2C_2 was also successfully dissolved in liquid ammonia to give a hydrogen acetylide ammoniate. Further investigations concerning the alkaline-earth-metal acetylides, NMR experiments of the acetylide–ammonia solutions, and experiments on the reactivity of the dissolved C_2^{2-} anions are under way.

Experimental Section

All of the preparations were carried out under an inert argon atmosphere using Schlenk and glove-box techniques. NH_3 (Linde) was dried by distillation from sodium and it was stored at −78 °C. The acetylides K_2C_2, Rb_2C_2, and Cs_2C_2 were prepared according to the known procedures.[5b,d]

Li_2C_2: Stoichiometric amounts of lithium and graphite were heated for 24 h at 1073 K in a sealed Ta ampoule.

$K_2C_2{\cdot}2NH_3$, $Rb_2C_2{\cdot}2NH_3$, $Cs_2C_2{\cdot}7NH_3$, $[Li(NH_3)_4]C_2H$**:** K_2C_2 (0.051 g, 0.50 mmol) was filled into a vacuum-dried Schlenk tube and dried ammonia (ca. 20 mL) was condensed at −78 °C. For Rb_2C_2 (0.066 g, 0.34 mmol), Cs_2C_2 (0.12 g, 0.41 mmol), and Li_2C_2 (0.250 g, 6.60 mmol), the same procedure was applied. The respective reaction vessels with suspensions of black solids in colorless liquids were first stored at −40 °C for several weeks and afterwards concentrated and stored at −75 °C to induce crystallization.

For X-ray investigations, the thermally unstable, air- and moisture-sensitive colorless crystals of $K_2C_2{\cdot}2NH_3$, $Rb_2C_2{\cdot}2NH_3$, $Cs_2C_2{\cdot}7NH_3$, and $[Li(NH_3)_4]C_2H$ were isolated from the mother liquor and directly transferred into a perfluoroether oil, which was cooled under a N_2 stream. By the use of the crystal-cap system the crystals were mounted onto a STOE-IPDS I diffractometer, where the data collection was performed at 123(2) K using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The data reduction was carried out with the STOE program package.[26] The structures were solved by direct methods using SHELXS-97.[27]

More details are given in the Supporting Information.

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[11] a) Structure refinement of $K_2C_2{\cdot}2NH_3$: $C_2H_6K_2N_2$, $M_r = 136.29\ g\,mol^{-1}$, crystal size $0.30 \times 0.25 \times 0.20\ mm^3$, monoclinic, space group $P2_1/n$, $a = 7.1658(13)$, $b = 5.5810(14)$, $c = 8.3330(15)$ Å, $\beta = 113.881(13)°$, $V = 304.73(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.485\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.422\ mm^{-1}$, $T = 123(2)$ K, $\theta = 3.18$–$26.48°$, measured/independent/observed ($I > 2\sigma(I)$) reflections 4392/605/534, $R_{int} = 0.0299$, R (F) (all data) $= 0.0231$, wR (F^2) (all data) $= 0.0478$, max./min. residual electron density: 0.212/−0.172 e Å^{-3}; b) Structure refinement of $Rb_2C_2{\cdot}2NH_3$: $C_2H_6Rb_2N_2$, $M_r = 229.02\ g\,mol^{-1}$, crystal size $0.20 \times 0.20 \times 0.05\ mm^3$, monoclinic, space group $C2/m$, $a = 10.864(2)$, $b = 4.9543(10)$, $c = 11.568(2)$ Å, $\beta = 99.93(3)°$, $V = 613.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.480\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 15.827\ mm^{-1}$, $T = 123(2)$ K, $\theta = 3.81$–$26.50°$, measured/independent/observed ($I > 2\sigma(I)$) reflections 4381/664/582, $R_{int} = 0.0472$, R (F) (all data) $= 0.0308$, wR (F^2) (all data) $= 0.0655$, max./min. residual electron density: 0.716/−0.813 e Å^{-3}; c) Structure refinement of $Cs_2C_2{\cdot}7NH_3$: $C_2H_{21}Cs_2N_7$, $M_r = 409.01\ g\,mol^{-1}$, crystal size $0.25 \times 0.20 \times 0.1\ mm^3$, monoclinic, space group $C2/m$, $a = 11.396(3)$, $b = 5.0728(8)$, $c = 11.184(2)$ Å, $\beta = 90.052(18)°$, $V = 646.5(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.096\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 5.609\ mm^{-1}$, $T = 123(2)$ K, $\theta = 3.58$–$28.07°$, measured/independent/observed ($I > 2\sigma(I)$) reflections 819/819/743, $R_{int} = 0.0414$, R (F) (all data) $= 0.0351$, wR (F^2) (all data) $= 0.1006$, max./min. residual electron density: 2.251/−0.884 e Å^{-3}; d) Structure refinement of $[Li(NH_3)_4]C_2H$: $C_2H_4Li_1N_1$, $M_r = 100.09\ g\,mol^{-1}$, crystal size $0.1 \times 0.1 \times 0.1\ mm^3$, tetragonal, space group $P4/n$, $a = 8.4019(12)$, $c = 5.041(1)$ Å, $V = 355.85(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.943\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.063\ mm^{-1}$, $T = 123(2)$ K, $\theta = 3.43$–$25.39°$, measured/independent/observed ($I > 2\sigma(I)$) reflections 2172/330/226, $R_{int} = 0.1888$, R (F) (all data) $= 0.0773$, wR (F^2) (all data) $= 0.1446$, max./min. residual electron density: 0.16/−0.15 e Å^{-3}. For a brief description of the data collection and the solution and refinement of the structures see Experimental Section. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 425116, 425117, 425118, and 425119.

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