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The Synthesis of Ternary Acetylides with Tellurium: Li$_2$TeC$_2$ and Na$_2$TeC$_2^{\dagger}$

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The synthesis of ternary acetylides Li$_2$TeC$_2$ and Na$_2$TeC$_2$ is presented as the first example of ternary acetylides with metalloid elements instead of transition metals. The synthesis was carried out by the direct reaction of the corresponding bialkali acetylides with tellurium powder in liquid ammonia. Alternatively, the synthesis of Na$_2$TeC$_2$ was also carried out by the direct reaction of tellurium powder and two equivalents of NaC$_2$H in liquid ammonia leading to Na$_2$TeC$_2$ and acetylene gas through an equilibrium containing the assumed NaTeC$_2$H molecules besides the reactants and the products. The resulting disordered crystalline materials were characterized by x-ray diffraction and Raman spectroscopy. Implications of these new syntheses on the synthesis of other ternary acetylides with metalloid elements and transition metals are also discussed.

1 Introduction

Ternary alkali metal (A) transition metal (M) acetylides with a general formula A$_2$MC$_2$ or AMC$_2$ have been the subject of research in inorganic and coordination chemistry for a few decades.$^{1-6}$ Ternary acetylides synthesized so far involve AMC$_2$ compounds with A ∈ {Li, Na, K, Rb, Cs} and M ∈ {Cu, Ag, Au} and A$_2$MC$_2$ compounds with A ∈ {Na, K, Rb, Cs} and M ∈ {Pt, Pd}. A major source of synthesis methods and characterization results on ternary acetylides is from the Ruschewitz group.$^{1,3,7-12}$ It was theoretically predicted in a recent publication by Terdik, Németh, Harkay et al.$^{13}$ that the photoemissive properties of Cs$_2$Te, an old photoemissive material with very high quantum efficiency, could be improved by introduction of an acetylenic unit to form the predicted Cs$_2$TeC$_2$ material. Related compounds, such as Na$_2$TeC$_2$, might have similarly advantageous photoemissive properties, such as high quantum-efficiency and reduced workfunction as calculated for the parent alkali tellurides. Existing A$_2$MC$_2$ ternary acetylides are built of linear polymeric chains with -M-C≡C- repeating units embedded in a matrix of alkali cations. The existence of such chains with -Te-C≡C-

repeating units was proposed by the above-mentioned theoretical study, motivated by knowledge of A$_2$MC$_2$ compounds. Analogous monomeric acetylenic tellurides/selenides/sulfides with the R-C≡C-(Te/Se/S)-C≡C-R’ structure have been known for decades.$^{9,14,15}$ Note, however, that in A$_2$MC$_2$ crystals the M atoms are formally neutral, and the -M-C≡C- repeating units carry a charge of negative two that is charge-balanced by two adjacent alkali cations, as compared to the charge neutral R-C≡C-(Te/Se/S)-C≡C-R’ species where the formal oxidation state of the chalcogen is +2. Alternatively, in the A$_2$TeC$_2$ systems developed in this study, the -Te-C≡C- repeating unit must carry a -2 charge. While binary transition metal acetylides with the formula MC$_2$ are well known explosives, their alkaliated versions AMC$_2$ and A$_2$MC$_2$ are not explosive. However, they are very air and moisture sensitive as they are strong reducing agents.$^{1}$ In fact, it is because of their strong reducing nature that LiAuC$_2$ and LiAgC$_2$, the only known Li-containing ternary acetylides,$^{7,8}$ have even been proposed as anode materials for Li-ion batteries.$^{16}$ Developing new syntheses of ternary acetylides with lighter and abundant transition metals or metalloids would allow for their practical consideration as anode materials in Li/Na-ion batteries. The goal of the present work was to develop an alternative synthesis to these intriguing materials, and determine the structure of a new class of tellurium containing ternary acetylides.

2 Experimental Section

2.1 Synthesis of Li$_2$TeC$_2$ from Li$_2$C$_2$ and Te

Li$_2$C$_2$ was synthesized by the reaction of Li metal and acetylene gas in liquid ammonia (lq-NH$_3$), followed by spontaneous disproportionation of LiC$_2$H to Li$_2$C$_2$ and acetylene gas upon evapo-
tion of the ammonia, and warming to ambient temperature, as described e.g. in Ref. 3. In a N2 glovebox, tellurium powder (384 mg, 3 mmol) as obtained from Sigma-Aldrich (99.8 %) was mixed with Li2C2 powder (120 mg, 3.17 mmol, 5.5 % excess) in a flame-dried 100 ml Schlenk flask with a Teflon plug valve, then sealed and brought into a fume hood. NH3 gas from a tank was condensed at ≈-60°C until it fully covered the solid reactants. The chilling of the flask was carried out in an acetone bath placed in a sonicator bay (Branson Model 3510 Ultrasonic Cleaner) through a coil attached to an electric laboratory chiller. Sonication of the reactants was started when they were completely covered by lq-NH3 gas from a tank and brought into a fume hood. NH3 gas was released by warming to ambient temperature, as described in Ref. 3.

Dependably swirled by hand and lifted out of the bath to confirm the disappearance of the Te powder at the bottom of the flask. Dependent on the concentration of the reactants in the lq-NH3, complete consumption of the Te typically took 10-30 minutes. The color of the reaction mixture gradually changed from purple to violet and finally to yellow. When the Te was fully consumed, the flask was gradually warmed to room temperature and the NH3 carefully evaporated. The flask was then sealed under a NH3 atmosphere and brought into the glove box for handling and storage.

2.2 Synthesis of Na2TeC2 from Na2C2 and Te

Na2C2 was synthesized by the reaction of elemental sodium and acetylene gas in lq-NH3 followed by heating the resulting NaC2H at 155 °C under vacuum as described in Ref. 17. The reaction of Te powder (384 mg, 3 mmol) with Na2C2 powder (220 mg, 3.14 mmol, 5 % excess) in lq-NH3 was carried out analogously to that of the above described synthesis of Li2TeC2. The resulting product is a yellow powder that also has to be handled in an inert atmosphere.

2.3 Synthesis of Na2TeC2 from NaC2H and Te

NaC2H was synthesized by the direct reaction of Na (200 mg, 8.70 mmol) with acetylene gas in lq-NH3 using a 100 ml Schlenk flask as above. Tellurium powder (520 mg, 4.06 mmol) was added to the dry NaC2H under protective flow of NH3 gas and lq-NH3 was condensed again on the reactants. The flask was occasionally manually swirled to allow for better mixing of the reactants. The Te powder was consumed in about 10 minutes without sonication producing a yellowish solution with some yellowish precipitates. The NH3 solvent was carefully evaporated and a pale yellow powder obtained. The sealed Schlenk flask was brought in the glove box and its contents were scraped into a mortar and ground whereby they became a yellow powder. Powder x-ray diffraction confirms that the materials obtained by the two different syntheses of Na2TeC2 are identical.

2.4 Synthesis of Tellurium Acetylide, TeC2

We have also attempted to synthesize the binary acetylide TeC2 polymer by the polycondensation reaction of diiodoacetylene18 and lithium telluride19 in dry tetrahydrofuran, according to

$$nI - C≡C - I + nLi_2Te \rightarrow (-Te - C≡C-)_n + 2nLiI.$$  (1)

The reaction product was a metallic gray powder that was extremely sensitive to mechanical agitation after being washed with water and diethyl ether on filter paper. When dry, this material violently decomposed upon contact with a spatula. Because of its explosivity that is similar to that observed in transition metal acetylides, this product could not be characterized.

2.5 Synthesis of Ph-C≡C-Te-C≡C-Ph and its double lithiated form

Bis(phenylethynyl)telluride, Ph-C≡C-Te-C≡C-Ph, was synthesized following the procedure of Ref. 20, starting from phenylacetylene (Sigma Aldrich). We have also attempted to synthesize its double lithiated form, in analogy to the A2TeC2 ternary acetylides, reacting Li-Ph-acetylide (Ph-C≡C-Li+) with Te powder in a 2:1 molar ratio in a sonicated dry THF solution. After about 24 hours of sonication all the Te powder was consumed. Evaporation of THF resulted in a yellow powder which turned out to be a 1:1 molar mixture of Ph-C≡C-TeLi+ and unreacted Ph-C≡CLi+, as characterized by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. This indicates that the hypothesized salt Li2[Ph-C≡C-Te-C≡C-Ph] does not form, and the negatively charged C≡C-Te-C≡C- structural units are stable only in the A2TeC2 ternary acetylides.

2.6 X-ray diffraction based characterization

Powder x-ray diffraction (XRD) spectra of the materials produced were obtained on a Bruker D2 Phaser benchtop XRD system using Cu-Kα1 radiation at 1.5406 Å wavelength, at room temperature. An air-tight PMMA specimen holder with a dome (Bruker A100B33) was used to hold the air-sensitive materials during the measurements. This sample holder adds a large background to the measured spectra between 15 and 25 (°) 2θ values. Note that XRD data for 2θ values smaller than those shown in Figs. 1 and 2 are all due to the sample holder, including a sharper peak at about 13 and a broader one at about 10 (°) 2θ. Crystal structures were refined using the GSAS software package.21

2.7 EXAFS based characterization

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy measurements were carried out on Ph-C≡C-Te-C≡C-Ph and its double lithiated form at the Te Kα edge using synchrotron radiation at the MRCAT (Sector 10) beamline of the APS facility at Argonne National Laboratory. Data was processed using the IFEFFIT-based programs Athena and Artemis.22,23

2.8 Raman spectroscopy

Raman spectra of Li2TeC2 and Na2TeC2 were measured at the Battery Post-Test Facility and the Center for Nanoscale Materials of Argonne National Laboratory, using a 514 nm laser excitation in a Renishaw inVia Raman Microprobe. Both materials decomposed to some extent during the measurement as indicated by
color change from yellow to brown. Na₂TeC₂ was less sensitive to laser-illumination and its spectrum was recorded with the C≡C stretching mode identified. In the Raman spectrum of the Li₂TeC₂ sample no C≡C stretching mode was observed. This could be either due to the Raman inactivity of the C≡C stretching mode in Li₂TeC₂, or more likely due to the decomposition of the sample in the illuminated spots. The formation of amorphous tellurium was also detected in both materials as a product of decomposition. In addition to that, some smaller amount of crystalline tellurium was also observed in the decomposition product of Li₂TeC₂. Further details of the Raman spectroscopic measurement are given in the supplementary material²⁴ and in Ref. 25.

3 Results and Discussion

All previously known ternary acetylides of the A₂M₂C₂ type were synthesized by the solid state reaction of the corresponding bialkali acetylides and Pt or Pd sponges⁹-¹¹:

\[ A_2C_2 + M \rightarrow A_2M_2C_2. \]  

As our initial attempts to follow the solid state reaction method failed for the direct reaction of tellurium powder with Li₂C₂, we had been looking for a suitable solvent to carry out the same reaction. As our initial attempts to follow the solid state reaction method failed for the direct reaction of tellurium powder with Li₂C₂, we had been looking for a suitable solvent to carry out the same reaction. A recent article by the Ruschewitz group pointed out that (b)alkali acetylides actually dissolve to some extent in liquid ammonia (lq-NH₃)¹². The same study also suggested that lq-NH₃ might be a suitable reaction medium for the synthesis of ternary acetylides. Motivated by this publication, we attempted the direct reaction of Te powder with slight molar excess of Li₂C₂ or Na₂C₂ in lq-NH₃. The rather quick dissolution of the Te powder during the reaction indicated the reaction of the dialkali acetylides with the Te metal, as no dissolution occurs in the absence of the acetylides. When run in an ultrasonicator, the Te was completely consumed in 10-30 minutes, depending on the concentration of the reactants. Ultrasonicication shortens the time needed for completing the consumption of Te powder by the dialkali acetylide, as compared to simple stirring (2-3 hours). We have used various temperatures from -80 to -35 °C and the reaction always completed very quickly when sonication was used. We have also tried using dry tetrahydrofuran and diethyl ether as a reaction solvent but these proved far inferior to lq-NH₃ and resulted only in some discoloration of the reactants even after hours of sonication.

The synthesis starts with the condensation of ammonia onto a mix of the Te and dialkali acetylide powder in a suitable, dry reaction vessel, such as a Schlenk flask. In the initial phase of the condensation, when there is only a small amount of lq-NH₃ present, purple/violet/red colors can be observed in the reaction mixture. These colors are typical indicators of polytelluride cluster anions that dissolve well in lq-NH₃, as known for a century¹⁹. Such polytelluride anions may consist of tens of Te atoms in a single cluster carrying typically only one negative charge or two¹⁹. In the case of our reactions, the charge of these Te clusters may only come from acetylide ions that attack the Te powder from the solution and split it up into cluster anions with attached acetylide units that dissolve in lq-NH₃. As the dissolution of binary acetylides in lq-NH₃ is very limited¹², one might expect a slow reaction. However, the small amount of dissolved acetylides is sufficient to solubilize all the tellurium powder and then it will be the dissolved polytelluride anions that attack the solid crystallites of dialkali acetylides to further split the polytelluride anions until all acetylide ions are attached to Te atoms or clusters. Thus, the solubility of polytelluride ions allows for an autocatalytic process and the reaction goes quickly even at low temperature, especially when sonication assists the mixing of the reactants and their attacks on each other.

The final product is a colloid of yellow Li₂TeC₂ or Na₂TeC₂ crystallites in lq-NH₃, which must be stored air-free after the evaporation of NH₃ and handled in a glove-box, as the products are very air and moisture sensitive, similar to their transition metal analogues.

The application of large (around 50 %) molar excess Te instead of excess acetylide results in a cherry red solution of dissolved species. In this case the complete dissolution of the Te powder may take a longer period of sonication and is believed to produce polytelluride ions with attached acetylide units.

While Li₂C₂ is easy to produce due to the spontaneous disproportionation of LiC₂H at room temperature, the production of heavier dialkali acetylides is increasingly cumbersome, especially for A ∈ (K, Rb, Cs) as it involves high temperature heating of monoalkali acetylides mixed with alkali metals in high vacuum³,¹². To avoid the direct use of dialkali acetylides we have developed an alternative synthesis based on monoalkali acetylides only. It consists of first reacting the Te powder with two molar equivalent of monoalkali acetylides according to

\[ 2AC₂H + Te \rightarrow ATeC₂H + AC₂H \]  

that is followed by the disproportionation of the resulting mixture:

\[ ATeC₂H + AC₂H \rightarrow A₂TeC₂ + H₂C₂ \uparrow. \]  

The first step of this reaction is familiar from analogous acetylenic organo-telluride reactions when the H of ATeC₂H is replaced by an organic functional group, typically an arene¹⁴,¹⁵,²⁰. The second step may largely complete when the solvent NH₃ is evaporated along with the acetylene gas, with the possibility that the rest of the acetylene gas is removed when the product is ground in a mortar. A repeated condensation of NH₃ and sonication of the mixture, followed by repeated evaporation of NH₃, helps to better mix the reaction components and remove as much residual acetylene gas as possible, before grinding the product in a mortar. We have not characterized ATeC₂H, as the above two reactions are part of an equilibrium and the isolation of ATeC₂H appeared difficult, if at all possible. The identity of the products for both Na₂TeC₂ syntheses are indicated by overlapping powder x-ray diffraction (XRD) spectra. The monoalkali acetylide based synthesis of ternary acetylides may be applicable to the synthesis of a wide variety of ternary acetylides avoiding the cumbersome production of heavier dialkali acetylides and the use of high-temperature solid state reactions.
Powder XRD spectra of Li$_2$TeC$_2$ and Na$_2$TeC$_2$ as well as the comparison of XRD patterns of Na$_2$TeC$_2$ made by the two different synthesis routes described above are shown in Figures 1, 2 and 3, respectively. The XRD spectra consist of a few broad peaks in the case of both compounds. The broadness of the peaks is not a consequence of the resolution of the measurements, as the Bruker apparatus used in taking the XRD spectra is regularly used to produce good quality powder XRD spectra. Instead, the broadness off the peaks is an indication of disordered crystalline materials where the heavy tellurium atoms form a crystalline structure that is filled with very disordered acetylide and alkali ions, as discussed in the following. DFT calculations strongly support the fitted structure for Na$_2$TeC$_2$, while for Li$_2$TeC$_2$ there is a larger deviation, the origins of which will be discussed below.

The main geometric parameters of Li$_2$TeC$_2$ and Na$_2$TeC$_2$, as obtained from Rietveld fitting of XRD data, are listed in Table 1. Full details of the fitting are available as supplementary material. For comparison, also the DFT-predicted structural parameters and those of the related ternary acetylides Na$_2$PdC$_2$ and Na$_2$PtC$_2$ are listed. Note that XRD data for 2θ values smaller than those shown in Figs. 1 and 2 are all due to the sample holder, including a sharper peak at about 13 and a broader one at about 10 (°) 2θ. Figures 4 and 5 display the fitted structures of Li$_2$TeC$_2$ and Na$_2$TeC$_2$, respectively. The space group of Li$_2$TeC$_2$ is P$\overline{3}$m1, identical with the space group of all known A$_2$MC$_2$ (M=Pt,Pd; A=Na,K,Rb,Cs) compounds. The space group of Na$_2$TeC$_2$, however, is I$\overline{4}$/mmm, representing a new structure in ternary acetylides. Also note that the fitting of Na$_2$TeC$_2$ data identified two phases, a major one of the actual Na$_2$TeC$_2$ material with I$\overline{4}$/mmm space group and a minor one of the unreacted excess Na$_2$C$_2$ used in the synthesis.

The C≡C distance in Li$_2$TeC$_2$ is 1.044 Å, interpreted as a projection of a wobbling C≡C dumbbell onto the c axis, therefore it is shorter than an acetylenic bond (C≡C distance is 1.203 Å in acetylene gas). The C≡C distance in Na$_2$TeC$_2$, as projected on the a and b axes, is 1.208 Å very close to that in acetylene. The wobbling motion of the C≡C dumbbell and its effect on the projected C≡C distance has also been observed in other ternary acetylides, such as K$_2$PdC$_2$. The short, 1.272 Å, Te-C distance in Li$_2$TeC$_2$ should also be interpreted as a projected distance, while the long, 2.333 Å, Te-C distance in Na$_2$TeC$_2$ is closer to expectations based on DFT predictions. The Te-C distance in Na$_2$TeC$_2$ is 2.333 Å, which is somewhat larger than that in Na$_2$PdC$_2$ but smaller than that in Na$_2$PtC$_2$, while it is about a 100 cm$^{-1}$ greater than that in the starting material Na$_2$C$_2$. The C≡C bond length in Na$_2$TeC$_2$ is shorter than in Na$_2$PdC$_2$ or Na$_2$PtC$_2$, this is also indicated by the greater vibrational wavenumber.

The C≡C stretching wavenumber of Na$_2$TeC$_2$ was measured by Raman spectroscopy and was found to be 1939 cm$^{-1}$. This value is similar to that observed in acetylene gas and it is greater than that observed in Na$_2$PdC$_2$ but smaller than that in Na$_2$PtC$_2$, while it is about a 100 cm$^{-1}$ greater than that in the starting material Na$_2$C$_2$. The Te-C distance in Na$_2$TeC$_2$ is 2.333 Å, which is somewhat larger than that in Na$_2$PtC$_2$, for a more precise determination of the Li and C positions, as Te has a much larger x-ray scattering factor. The measurement of $^{13}$C NMR spectra would be helpful in the characterization of the types of carbon atoms present.

The above types of additional characterizations could not be
carried out in the present work primarily for reasons of great air-sensitivity of the product materials. They will be subject of forthcoming investigations. However, we are still confident that we have identified the title new compounds solely on the basis of the presented XRD data and through the control of the stoichiometries of the reactants. The XRD spectra of related compounds, such as $A_2O$, $AOH$, $A_2Te$, $A_2Te_2$, $Te$, $A_2C_2$ and $AC_2H$ ($A = Li$, Na, with the exception of $Li_2Te_2$ that is not known$^{19}$) are so clearly distinct from the observed XRD spectra, that none of them was found to be present in the syntheses products, except a small amount of the alkali acetylides used in excess as reactants and small amount of LiOH contamination of the $Li_2C_2$ used$^{24}$.

We have not taken elemental analysis of the products either, as the purity of the reagents was confirmed by XRD analysis and the solvent lq-NH$_3$ is not expected to react with them at the low temperatures applied and is unlikely to form stable complexes with Li$^+$ or Na$^+$ at room temperature as ammonia complexes of alkali acetylides are known to exist only at the low temperatures of lq-NH$_3$,$^{12}$ and would decompose when warmed up to room temperature. Therefore the total stoichiometry of the products should be the same as that of the reactants with the exception of the reaction using Na$_2C_2H$ as reactant. In this latter case, however, the identity of the diffraction patterns shown in Fig. 3 indicates identical composition of the products of the two different syntheses referenced in the same Figure, which makes the disproportionation of Na$_2C_2H$ to Na$_2C_2$ and H$_2C_2$ as described in Eqs. 3 and 4 the only possible explanation of this reaction even without the explicit detection of H$_2C_2$ in the gases when the lq-NH$_3$ solvent is evaporated.

It is well known that Zintl anions (polyanions) of heavier p-field elements, such as Te, Se, As, Sb, Bi, Pb, etc. are highly soluble in lq-NH$_3$ (for reviews see e.g. Refs. 26,27). Such polyanions have also been observed with some transition metal elements, such as Hg$^{26}$. This solubility of the Zintl anions in lq-NH$_3$ suggests that more ternary acetylides with metalloid and transition metal elements may be synthesized in lq-NH$_3$ following analogous procedures to the ones described herein for Te-containing ternary acetylides. In principle, these procedures may work also for transition metals if the transition metal starting material is provided in the form of sufficiently small polyatomic clusters, for example in the form of pyrophoric iron, nickel, manganese, etc. This may provide a practical route for the production and use of ternary acetylides, for example as anode materials in Li-ion batteries.

In order to test whether the charged bis(ethynyl) tellurides exist in a molecular form as well, we have synthesized Ph-C≡C-Te-C≡C-Ph following Ref. 20 and its hypothetical double lithiated form, $Li_2[Ph-C≡C-Te-C≡C-Ph]$, by the direct reaction of Ph-C≡C-Li$^+$ with Te powder in a 2:1 molar ratio in sonicated dry THF solution. Figure 6 shows a comparison of the Te K-edge EXAFS spectra of the two materials. The spectrum of Ph-C≡C-Te-C≡C-Ph can be modeled up to $R = 3$ Å by nominal structure which has two C≡C groups surrounding the Te absorber (see supplementary material for details, Ref. 24). However the spectrum of $Li_2[Ph-C≡C-Te-C≡C-Ph]$ shows ca. 0.8 C≡C groups surrounding each Te atom on average. This indicates that the product of the latter reaction is a less than 1:1 molar mixture of Ph-C≡C-Te$^-Li^+$ and unreacted Ph-C≡C-Te-C≡C-Ph, see Figure 6. This suggests that the negatively charged -C≡C-Te-C≡C- bonding system exists only in the crystals of $A_2TeC_2$ ternary acetylides and not in molecular forms.

It is difficult to tell without specific experimental studies, what the charge of the tellurium is in the $A_2TeC_2$ systems. A suitable method of investigation could be photoelectron spectroscopy. However, it is reasonable to assume that the charge of the alkali cations is +1 and therefore the combined charge of the Te and the acetylide ion should be -2. The negative charge of the acetylide ion can potentially be partially distributed to tellurium, however, this would come with a significant elongation of the C-C bond of the acetylide ion, which does not seem to be the case. Therefore, Te(0) is what one would expect based on these simple considerations.

While the ternary acetylides synthesized in the present work may display many interesting physical properties, such as those predicted in Ref. 13 by Terdik, Németh, Harkay, et al., the present work was intended to discuss solely the synthesis of these new materials. The examination of their electronic properties, such as charge distribution, workfunction, photoemissive quantum yield and battery electrode applications should be the subject of separate investigations. We believe that the synthesis methods described here are significantly new as they allow for a quick solvent-based synthesis of $A_2MC_2$ type ternary acetylides instead of the traditional high temperature solid state synthesis. The key enabler of the new synthesis methods is the solubility of acetylated polyanionic clusters of tellurium atoms (or potentially that of other metalloid or metal elements) in lq-NH$_3$, described in the present work for the first time in the literature. This development was also motivated by the recent observation of sparing solubility of acetylide ions in lq-NH$_3$ by the Ruschewitz-group.$^{12}$

### 4 Summary and Conclusions

We have described two efficient new synthesis methods for the production of ternary alkali metal tellurium acetylides, $Li_2TeC_2$ and $Na_2TeC_2$. The new syntheses methods are based on the reaction of binary alkali acetylides with tellurium in lq-NH$_3$, or on the reaction of tellurium powder with two equivalent of monoalkali acetylides in lq-NH$_3$ and letting the system disproportionate to the corresponding bialkali ternary acetylide and acetylene gas. This latter method avoids the cumbersome synthesis of heavier binary acetylides. The syntheses are significantly accelerated by ultrasonication. The colors of the reaction mixture point toward the existence of polyatomic tellurium anions with attached acetylene units dissolved in lq-NH$_3$ in earlier phases of the reactions. The good solubility of these polyanions in lq-NH$_3$ and the modest solubility of binary acetylides allow for fast reactions even at the low temperatures of the lq-NH$_3$ medium, especially when sonication is used, too. The ternary acetylides produced are the first examples of ternary acetylides with metalloid elements, as opposed to the numerous examples of previously synthesized ternary acetylides with Au, Ag, Cu, Pd and Pt. The structures of $Li_2TeC_2$ and $Na_2TeC_2$ are disordered crystalline ones, meaning that while the heavier Te atoms are arranged in a crystalline order, the much smaller acetylide units and alkali cations are largely
disordered. Furthermore, it is expected that these new syntheses may be used analogously to produce ternary acetylides with other metalloid and transition metal elements as well, provided that soluble polyatomic anions can be produced in early phases of the reactions.

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References

24. The following supplementary materials are available: 1. The cif files of the fitted crystal structures and the measured XRD spectra in xye format. 2. Details of the EXAFS analysis presented in this work. 3. Structural parameters as predicted by DFT calculations. 4. Details of the Raman spectroscopic measurements. 5. The XRD analysis of the composition of the Li2C2 samples.
Table 1 Selected crystallographic data\textsuperscript{24} of $A_2\text{TeC}_2$ ($A$=Li,Na). The P(C≡C) and P(\text{Te-C}) nearest neighbor distances are projections on the c axis, as the C≡C dumbbell carries out a wobbling motion, also observed in other ternary acetylides\textsuperscript{10}. Lengths are given in Å, cell volumes in Å\textsuperscript{3}, angles in degrees. DFT predicted structural parameters and structural parameters of related Na$_2$(Pd/Pt)C\textsubscript{2} compounds\textsuperscript{11} are also listed for comparison. The DFT methodology used is the same as in Ref. 13. XRD and ND refer to x-ray and neutron diffraction, respectively.

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<td>5.7340</td>
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<td>c</td>
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<td>5.874(4)</td>
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<td>α</td>
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<td>90.0</td>
<td>90.0</td>
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<tr>
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<td>99.38</td>
<td>202.60(14)</td>
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<tr>
<td>P(M-C)</td>
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<tr>
<td>P(C≡C)</td>
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<td>1.262</td>
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<tr>
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<td>2.982</td>
<td>3.284</td>
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<td>$R_p$</td>
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<td>0.034</td>
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<tr>
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<td>$\chi^2$</td>
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<td>2.269</td>
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<td>$(\Delta/\sigma)_{max}$</td>
<td>3.78</td>
<td>-</td>
<td>1.44</td>
<td>-</td>
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Table 2 Wavenumbers (cm\textsuperscript{-1}) of the C≡C stretching vibrations ($\tilde{\nu}_{C≡C}$) in Na$_2$TeC$_2$ (this work) and in a few binary and ternary acetylides (previously reported) as observed by Raman spectroscopy.

<table>
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<tr>
<th></th>
<th>Na$_2$TeC$_2$</th>
<th>H$_2$C$_2$</th>
<th>Na$_2$C$_2$</th>
<th>Na$_2$PdC$_2$</th>
<th>Na$_2$PtC$_2$</th>
<th>NaAgC$_2$</th>
<th>NaAuC$_2$</th>
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<tr>
<td>$\tilde{\nu}_{C≡C}$</td>
<td>1939</td>
<td>1974\textsuperscript{28}</td>
<td>1845\textsuperscript{29}</td>
<td>1862\textsuperscript{11}</td>
<td>1845\textsuperscript{11}</td>
<td>1965\textsuperscript{7}</td>
<td>1997\textsuperscript{8}</td>
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</table>
Fig. 1 Powder X-ray diffraction spectrum of Li$_2$TeC$_2$ (red), the corresponding Rietveld-fit (green) and the difference of experimental and fitted spectra (purple).
Fig. 2 Powder X-ray diffraction spectrum of Na₂TeC₂ (red), the corresponding Rietveld-fit (green) and the difference of experimental and fitted spectra (purple).
Fig. 3 Powder X-ray diffraction spectra of Na₂TeC₂ as obtained by two different synthesis methods. Synthesis (A): Na₂C₂ + Te → Na₂TeC₂.
Synthesis (B): 2 NaC₂H + Te → Na₂TeC₂ + C₂H₂.
Fig. 4 Structure of the \( \text{Li}_2\text{TeC}_2 \) crystal (space group \( \text{P}3\text{m}1 \)) as determined from the powder x-ray diffraction data. Color code: C - gray, Te - bronze, Li - violet.
Fig. 5 Structure of the Na$_2$TeC$_2$ crystal (space group I4/mmm) as determined from the powder x-ray diffraction data. Color code: C - gray, Te - bronze, Na - violet.
Fig. 6 Comparison of the Te K$_\alpha$ EXAFS spectra of Ph-C≡C-Te-C≡C-Ph and its hypothetical double lithiated form. The EXAFS intensities of the double lithiated form are approximately 40% of that of the unlihiated form, indicating that less than half of the phenylacetylene groups are bound to Te, i.e. the double lithiated form is a mixture of Ph-C≡C-Te$^-$ Li$^+$ and Ph-C≡C Li$^+$. 