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# The Synthesis of Ternary Acetylides with Tellurium: $Li_2TeC_2$ and $Na_2TeC_2$[†]

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The synthesis of ternary acetylides $Li_2TeC_2$ and $Na_2TeC_2$ 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 $Na_2TeC_2$ was also carried out by the direct reaction of tellurium powder and two equivalents of $NaC_2H$ in liquid ammonia leading to $Na_2TeC_2$ and acetylene gas through an equilibrium containing the assumed $NaTeC_2H$ 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 $A_2MC_2$ 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 $A_2MC_2$ 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 $Cs_2Te$, an old photoemissive material with very high quantum efficiency, could be improved by introduction of an acetylenic unit to form the predicted $Cs_2TeC_2$ material. Related compounds, such as $Na_2TeC_2$, might have similarly advantageous photoemissive properties, such as high quantum-efficiency and reduced workfunction as calculated for the parent alkali tellurides. Existing $A_2MC_2$ 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 $A_2MC_2$ compounds. Analogous monomeric acetylenic tellurides/selenides/sulfides with the R-C≡C-(Te/Se/S)-C≡C-R′ structure have been known for decades[4,14,15]. Note, however, that in $A_2MC_2$ 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 $A_2TeC_2$ 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 alkalinated versions $AMC_2$ and $A_2MC_2$ 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 $Li_2TeC_2$ from $Li_2C_2$ and Te

$Li_2C_2$ was synthesized by the reaction of Li metal and acetylene gas in liquid ammonia (lq-$NH_3$), followed by spontaneous disproportionation of $LiC_2H$ to $Li_2C_2$ and acetylene gas upon evapora-

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tion of the ammonia, and warming to ambient temperature, as described e.g. in Ref. 3. In a $N_2$ glovebox, tellurium powder (384 mg, 3 mmol) as obtained from Sigma-Aldrich (99.8 %) was mixed with $Li_2C_2$ 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. $NH_3$ 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-$NH_3$ (5-10 mL). The sonication and condensation of $NH_3$ (at a slightly higher than atmospheric pressure) continued until all the Te powder was consumed by the reaction. The flask was occasionally swirled by hand and lifted out of the bath to confirm the disappearance of the Te powder at the bottom of the flask. Depending on the concentration of the reactants in the lq-$NH_3$, 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 $NH_3$ carefully evaporated. The flask was then sealed under a $NH_3$ atmosphere and brought into the glove box for handling and storage.

### 2.2 Synthesis of $Na_2TeC_2$ from $Na_2C_2$ and Te

$Na_2C_2$ was synthesized by the reaction of elemental sodium and acetylene gas in lq-$NH_3$ followed by heating the resulting $NaC_2H$ at 155 °C under vacuum as described in Ref. 17. The reaction of Te powder (384 mg, 3 mmol) with $Na_2C_2$ powder (220 mg, 3.14 mmol, 5 % excess) in lq-$NH_3$ was carried out analogously to that of the above described synthesis of $Li_2TeC_2$. The resulting product is a yellow powder that also has to be handled in an inert atmosphere.

### 2.3 Synthesis of $Na_2TeC_2$ from $NaC_2H$ and Te

$NaC_2H$ was synthesized by the direct reaction of Na (200 mg, 8.70 mmol) with acetylene gas in lq-$NH_3$ using a 100 ml Schlenk flask as above. Tellurium powder (520 mg, 4.06 mmol) was added to the dry $NaC_2H$ under protective flow of $NH_3$ gas and lq-$NH_3$ 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 $NH_3$ 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 $Na_2TeC_2$ are identical.

### 2.4 Synthesis of Tellurium Acetylide, $TeC_2$

We have also attempted to synthesize the binary acetylide $TeC_2$ polymer by the polycondensation reaction of diiodoacetylene[18] and lithium telluride[19] in dry tetrahydrofuran, according to

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

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 explositivity 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 $A_2TeC_2$ 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-$Te^-Li^+$ and unreacted Ph-C≡$C^-Li^+$, as characterized by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. This indicates that the hypothesized salt $Li_2$[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 $A_2TeC_2$ 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-$K_{\alpha 1}$ 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 $K_\alpha$ 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 $Li_2TeC_2$ and $Na_2TeC_2$ 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. $Na_2TeC_2$ was less sensitive to laser-illumination and its spectrum was recorded with the C≡C stretching mode identified. In the Raman spectrum of the $Li_2TeC_2$ sample no C≡C stretching mode was observed. This could be either due to the Raman inactivity of the C≡C stretching mode in $Li_2TeC_2$, 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 $Li_2TeC_2$. Further details of the Raman spectroscopic measurement are given in the supplementary material[24] and in Ref. 25.

## 3 Results and Discussion

All previously known ternary acetylides of the $A_2MC_2$ type were synthesized by the solid state reaction of the corresponding bialkali acetylides and Pt or Pd sponges[9–11]:

$$A_2C_2 + M \rightarrow A_2MC_2. \tag{2}$$

As our initial attempts to follow the solid state reaction method failed for the direct reaction of tellurium powder with $Li_2C_2$, we had been looking for a suitable solvent to carry out the same reaction.

A recent article by the Ruschewitz group pointed out that (bi)alkali acetylides actually dissolve to some extent in liquid ammonia (lq-$NH_3$)[12]. The same study also suggested that lq-$NH_3$ 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 $Li_2C_2$ or $Na_2C_2$ in lq-$NH_3$. 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. Ultrasonication significantly shortens the time needed for completing the consumption of Te powder by the bialkali acetylide, as compared to simple stirring (2-3 hours). We have used various temperatures from -80 to -35 $^{o}$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-$NH_3$ 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 bialkali 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-$NH_3$ 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-$NH_3$, as known for a century[19]. Such polytelluride anions may consist of tens of Te atoms in a single cluster carrying typically only one negative charge or two[19]. 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-$NH_3$. As the dissolution of binary acetylides in lq-$NH_3$ is very limited[12], 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 bialkali 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 $Li_2TeC_2$ or $Na_2TeC_2$ crystallites in lq-$NH_3$, which must be stored air-free after the evaporation of $NH_3$ 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 $Li_2C_2$ is easy to produce due to the spontaneous disproportionation of $LiC_2H$ at room temperature, the production of heavier bialkali acetylides is increasingly cumbersome, especially for $A \in \{K, Rb, Cs\}$ as it involves high temperature heating of monoalkali acetylides mixed with alkali metals in high vacuum[3,12]. To avoid the direct use of bialkali 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

$$2AC_2H + Te \rightarrow ATeC_2H + AC_2H \tag{3}$$

that is followed by the disproportionation of the resulting mixture:

$$ATeC_2H + AC_2H \rightarrow A_2TeC_2 + H_2C_2 \uparrow . \tag{4}$$

The first step of this reaction is familiar from analogous acetylenic organo-telluride reactions when the H of $ATeC_2H$ is replaced by an organic functional group, typically an arene[14,15,20]. The second step may largely complete when the solvent $NH_3$ 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 $NH_3$ and sonication of the mixture, followed by repeated evaporation of $NH_3$ 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 $ATeC_2H$, as the above two reactions are part of an equilibrium and the isolation of $ATeC_2H$ appeared difficult, if at all possible. The identity of the products for both $Na_2TeC_2$ 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 bialkali acetylides and the use of high-temperature solid state reactions.

Powder XRD spectra of $Li_2TeC_2$ and $Na_2TeC_2$ as well as the comparison of XRD patterns of $Na_2TeC_2$ 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 $Na_2TeC_2$, while for $Li_2TeC_2$ there is a larger deviation, the origins of which will be discussed below.

The main geometric parameters of $Li_2TeC_2$ and $Na_2TeC_2$, as obtained from Rietveld fitting of XRD data, are listed in Table 1. Full details of the fitting are available as supplementary material[24]. For comparison, also the DFT-predicted structural parameters and those of the related ternary acetylides $Na_2PdC_2$ and $Na_2PtC_2$ 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 ($^o$) 2Θ. Figures 4 and 5 display the fitted structures of $Li_2TeC_2$ and $Na_2TeC_2$, respectively. The space group of $Li_2TeC_2$ is $P\bar{3}m1$, identical with the space group of all known $A_2MC_2$ (M=Pt,Pd; A=Na,K,Rb,Cs) compounds. The space group of $Na_2TeC_2$, however, is I4/mmm, representing a new structure in ternary acetylides. Also note that the fitting of $Na_2TeC_2$ data identified two phases, a major one of the actual $Na_2TeC_2$ material with I4/mmm space group and a minor one of the unreacted excess $Na_2C_2$ used in the synthesis.

The C≡C distance in $Li_2TeC_2$ 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 $Na_2TeC_2$, 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 $K_2PdC_2$[10]. The short, 1.727 Å, Te-C distance in $Li_2TeC_2$ should also be interpreted as a projected distance, while the long, 2.333 Å, Te-C distance in $Na_2TeC_2$ is closer to expectations based on DFT predictions[13]. The Te-C distance in bis[(4-methylphenyl) ethynyl] telluride is 2.045 Å[20], while it is expected to be about 2.4 Å in ternary acetylides with Te on the basis of DFT calculations, assuming the $P\bar{3}m1$ space group[13]. The observed and DFT-predicted lattice parameters of $Li_2TeC_2$ differ a lot: the observed a = b = 6.2981 Å and the c = 4.4987 Å values appear to be approximately reversed as compared to the predictions. As a consequence of this change in the lattice parameters, the Li-Te and Li-C distances will also become much longer than predicted: 3.851 and 3.665 Å, instead of 2.982 and 2.636 Å, respectively, while the Li-Li distances remain relatively close to the DFT-predicted values: 4.131 Å (observed) vs 4.356 Å (predicted).

The long experimental a and b lattice parameters in $Li_2TeC_2$ suggest that the Te-C≡C-Te units actually run along the a and b axes instead of the c, while the short c parameter (twice about 2.25 Å) suggests Li ions complexed by acetylide ions along the c direction, with the acetylide ions lying in the a or b directions. We have explored such structural models with 1/6 probability for Li and carbon positions using the P6/mmm space group or closely related ones, however the resulting fits were significantly less good than the one with the $P\bar{3}m1$ space group. At present, our best explanation of the surprisingly large a/c ratio in $Li_2TeC_2$ and the large Li-Te and Li-C as well as the short Te-C distances is based on the above mentioned wobbling motion of the C≡C unit around the c-axis in the $P\bar{3}m1$ space group and this may also explain the broad peaks in the XRD spectra.

In the case of $Na_2TeC_2$, the DFT-predicted structure is fairly close to the XRD one. In fact a simple bcc arrangement of the Te atoms could already fit the powder XRD spectrum well. Therefore the tetragonal splitting that we suggest, i.e. the transition from a simple bcc lattice to I4/mmm space group, is based on the DFT calculations, even though it leads to a somewhat improved fit of the XRD data. This structure suggests that the acetylide ions may be oriented with near equal probability along each of the a, b and c axes. Such a flipping of orientation of the acetylide units in $Na_2TeC_2$ would create a disordered I4/mmm structure that resembles to a true bcc structure. We have also attempted to create a model to describe this directional flipping of the acetylide units through partial filling of the corresponding directional alternatives, however these models turned out to fit the XRD data less well than the simple I4/mmm structure.

The broadness of the observed XRD spectral lines may partially also be attributed to crystal defects that may occur due to the low temperature of the synthesis where the crystal structure can not anneal well.

The C≡C stretching wavenumber of $Na_2TeC_2$ 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 $Na_2(Pd/Pt)C_2$ but smaller than that in $Na(Ag/Au)C_2$, while it is about a 100 $cm^{-1}$ greater than that in the starting material $Na_2C_2$ . See Table 2 for comparison.

The Te-C distance in $Na_2TeC_2$ is 2.333 Å, which is somewhat larger than the (Pd/Pt)-C distances in $Na_2(Pd/Pt)C_2$ (≈ 2 Å), and in bis[(4-methylphenyl) ethynyl] telluride (2.045 Å)[20]. The C≡C bond length in $Na_2TeC_2$ is shorter than in $Na_2(Pd/Pt)C_2$, this is also indicated by the greater vibrational wavenumber.

In the present phase of our research on ternary acetylides with tellurium, our only method of characterization (besides Raman spectroscopy) was x-ray diffraction of the freshly made samples shortly after the synthesis, using an air-tight PMMA sample holder. We have also attempted to obtain synchrotron XRD data of the same samples: unfortunately, the samples partially decomposed during the storing and handling, this was indicated by significant additional peaks in the synchrotron XRD spectra, as compared to the locally measured ones. Neutron diffraction would also be very useful, especially for $Li_2TeC_2$, for a more precise determination of the Li and C positions, as Te has a much greater 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 $NaC_2H$ 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 $NaC_2H$ 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≡$C^-Li^+$, 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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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 $Li_2C_2$ samples.

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**Table 1** Selected crystallographic data[24] of $A_2TeC_2$ (A=Li,Na). The P(C≡C) and P(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[10]. Lengths are given in Å, cell volumes in Å$^3$, angles in degrees. DFT predicted structural parameters and structural parameters of related $Na_2(Pd/Pt)C_2$ compounds[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 neuron diffraction, respectively.

| | $Li_2TeC_2$ | | $Na_2TeC_2$ | | $Na_2PdC_2$[11] | $Na_2PtC_2$[11] |
|---|---|---|---|---|---|---|
| Space group | $P\bar{3}m1$ | | I4/mmm | | $P\bar{3}m1$ | $P\bar{3}m1$ |
| data type | XRD | DFT | XRD | DFT | ND | ND |
| a | 6.2981(14) | 4.3556 | 5.8727(7) | 5.7340 | 4.4638 | 4.5031 |
| b | 6.2981(14) | 4.3556 | 5.8727(7) | 5.7340 | 4.4638 | 4.5031 |
| c | 4.4987(9) | 6.0533 | 5.874(4) | 6.1357 | 5.2668 | 5.2050 |
| $\alpha$ | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 |
| $\beta$ | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 |
| $\gamma$ | 120.0 | 120.0 | 90.0 | 90.0 | 120.0 | 120.0 |
| $V_{cell}$ | 154.52(9) | 99.38 | 202.60(14) | 207.78 | 90.88 | 91.40 |
| P(M-C) | 1.727 | 2.395 | 2.333 | 2.437 | 2.002 | 1.958 |
| P(C≡C) | 1.044 | 1.264 | 1.208 | 1.262 | 1.263 | 1.289 |
| A-A | 4.131 | 4.356 | 2.936 | 3.068 | 3.910 | 3.867 |
| A-C | 3.665 | 2.636 | 3.061 | 3.006 | 2.631 | 2.652 |
| A-Te | 3.851 | 2.982 | 3.284 | 3.251 | 2.968 | 2.967 |
| No. of data points | 2226 | - | 4205 | - | - | - |
| No. of fitting params. | 25 | - | 19 | - | - | - |
| $R_p$ | 0.029 | - | 0.034 | - | - | - |
| $R_{wp}$ | 0.040 | - | 0.046 | - | - | - |
| $R_{exp}$ | 0.022 | - | 0.028 | - | - | - |
| $\chi^2$ | 3.312 | - | 2.269 | - | - | - |
| $(\Delta/\sigma)_{max}$ | 3.78 | - | 1.44 | - | - | - |

**Table 2** Wavenumbers (cm$^{-1}$) of the C≡C stretching vibrations ($\tilde{\nu}_{C\equiv C}$) in $Na_2TeC_2$ (this work) and in a few binary and ternary acetylides (previously reported) as observed by Raman spectroscopy.

| | $Na_2TeC_2$ | $H_2C_2$ | $Na_2C_2$ | $Na_2PdC_2$ | $Na_2PtC_2$ | $NaAgC_2$ | $NaAuC_2$ |
|---|---|---|---|---|---|---|---|
| $\tilde{\nu}_{C\equiv C}$ | 1939 | 1974[28] | 1845[29] | 1862[11] | 1845[11] | 1965[7] | 1997[8] |

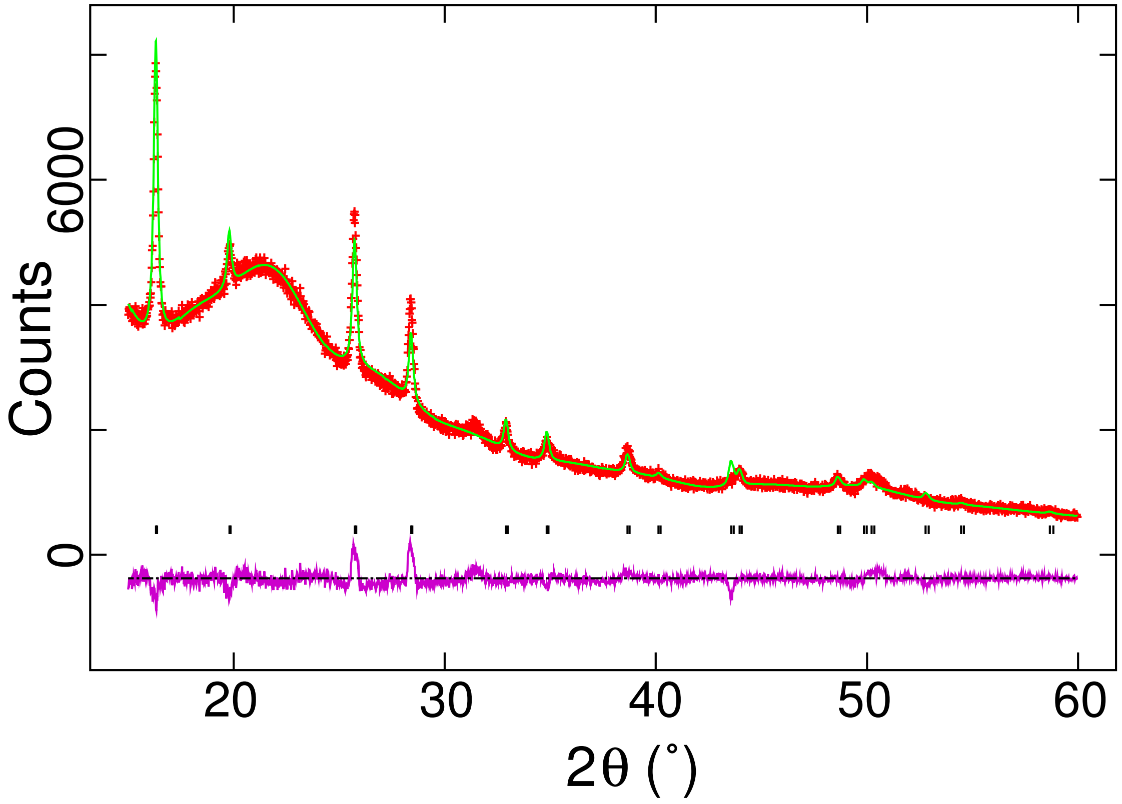

**Fig. 1** Powder X-ray diffraction spectrum of $Li_2TeC_2$ (red), the corresponding Rietveld-fit (green) and the difference of experimental and fitted spectra (purple).

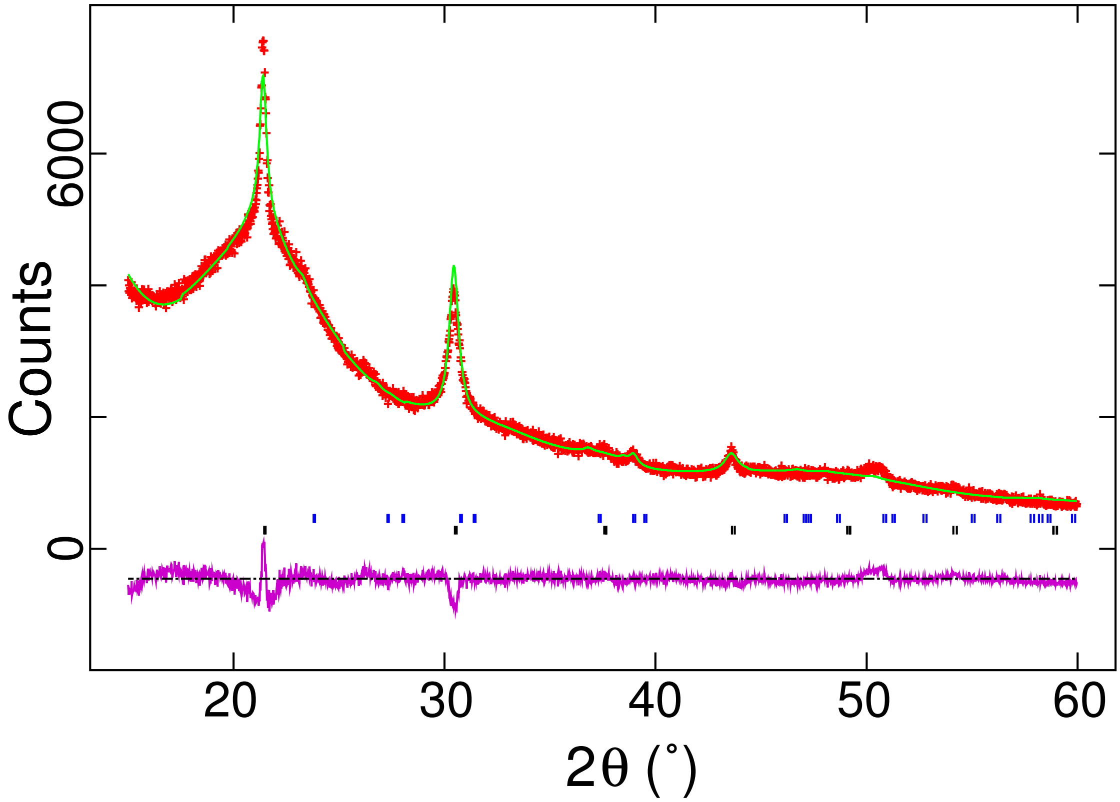

**Fig. 2** Powder X-ray diffraction spectrum of $Na_2TeC_2$ (red), the corresponding Rietveld-fit (green) and the difference of experimental and fitted spectra (purple).

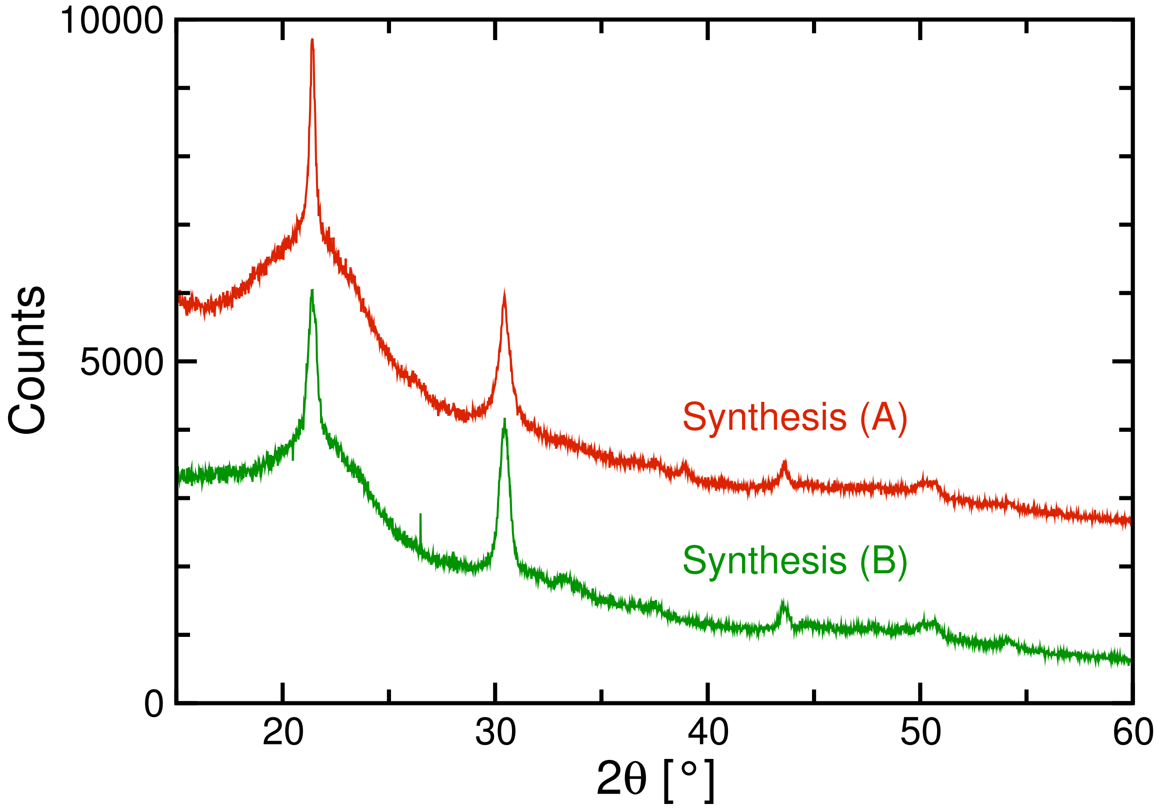

**Fig. 3** Powder X-ray diffraction spectra of $Na_2TeC_2$ as obtained by two different synthesis methods. Synthesis (A): $Na_2C_2 + Te \rightarrow Na_2TeC_2$. Synthesis (B): $2\ NaC_2H + Te \rightarrow Na_2TeC_2 + C_2H_2$.

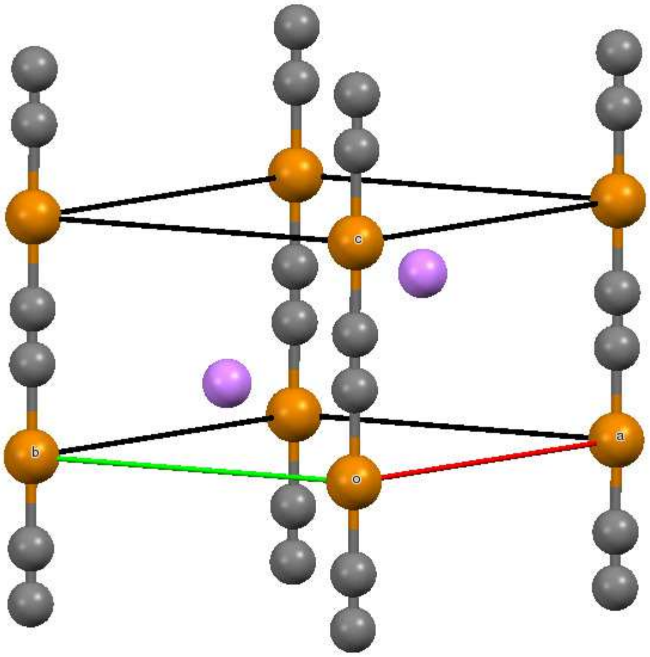

**Fig. 4** Stucture of the $Li_2TeC_2$ crystal (space group $P\overline{3}m1$) as determined from the powder x-ray diffraction data. Color code: C - gray, Te - bronze, Li - violet.

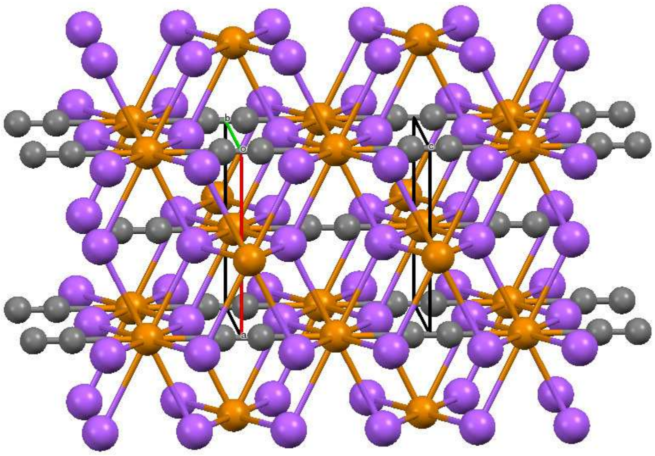

**Fig. 5** Stucture of the $Na_2TeC_2$ crystal (space group I4/mmm) as determined from the powder x-ray diffraction data. Color code: C - gray, Te - bronze, Na - violet.

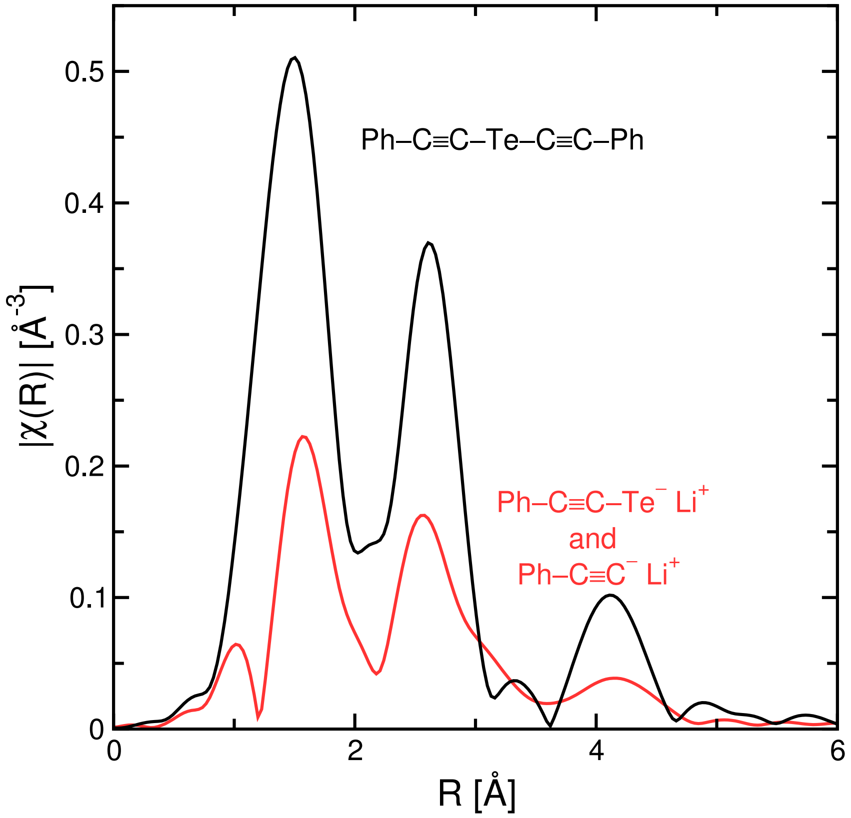

**Fig. 6** Comparison of the Te $K_\alpha$ EXAFS spectra of Ph-C≡C-Te-C≡C-Ph and its hypothetical double lithiated form. The EXAFS intensities of the double lithiated form are approximately 40% of that of the unlithiated form, indicating that less than half of the phenylacetylene groups are bound to Te, i.e. the double lithiated form is a mixture of Ph-C≡C-Te$^-$Li$^+$ and Ph-C≡C$^-$Li$^+$.