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Ternary Alkali Metal Transition Metal Acetylides

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Abstract. The first alkali metal transition metal acetylides of general composition $A_2M^0C_2$ ($A = Na - Cs$, $M^0 = Pd, Pt$) were obtained by solid state reactions of alkali metal acetylides with palladium and platinum. They are characterized by ${}^\infty[M^0(C_2)_{2/2}^{2-}]$ chains, which are separated by alkali metal ions. Analogous ${}^\infty[M^I(C_2)_{2/2}^-]$ chains also separated by alkali metal ions are the characteristic structural feature of acetylides of composition AM^IC_2 , which are accessible by reacting AC_2H with M^II in liquid ammonia ($A = Li - Cs$, $M^I = Cu, Ag, Au$). Despite their structural similarities they possess different properties, as acetylides of composition $A_2M^0C_2$ are semiconductors with very small indirect band gaps and slightly extended C–C distances compared to a C–C triple bond, whereas acetylides of composition AM^IC_2 show a typical salt-like behavior with C–C distances close to the expected value for a C–C triple bond of 120 pm. But with the help of simple chemical models these differences can be made plausible. Furthermore, it is shown that only by a combination of different methods (powder diffraction with X-rays and neutrons, solid state NMR spectroscopy, Raman spectroscopy) it was possible to characterize this new class of compounds structurally and chemically.

Keywords: Acetylides, Alkali metal, Metal carbides, Powder diffraction, Solid state NMR spectroscopy

Ternäre Alkalimetallübergangsmetallacetylide.

Inhaltsübersicht. Durch Festkörperreaktionen von Alkalimetallacetylidien mit Palladium bzw. Platin konnten die ersten ternären Alkalimetallübergangsmetallacetylide mit der allgemeinen Zusammensetzung $A_2M^0C_2$ ($A = Na - Cs$, $M^0 = Pd, Pt$) erhalten werden. Sie sind durch $\infty[M^0(C_2)_{2/2}^{2-}]$ -Ketten charakterisiert, die von den Alkalimetallionen separiert werden. Analoge $\infty[M^I(C_2)_{2/2}^{-}]$ -Ketten, zwischen denen Alkalimetallionen liegen, sind das Strukturmerkmal von Acetylidien der Zusammensetzung AM^IC_2 , die durch Reaktionen von AC_2H mit M^I in flüssigem Ammoniak zugänglich sind ($A = Li - Cs$, $M^I = Cu, Ag, Au$). Trotz ihrer strukturellen Ähnlichkeit haben die Verbindungen sich deutlich voneinander unterscheidende Eigenschaften, da die Acetylide der Zusammensetzung $A_2M^0C_2$ Halbleiter mit sehr kleinen indirekten Bandlücken und im Vergleich zur Dreifachbindung aufgeweiteten C–C-Abständen sind, wohingegen die Acetylide der Zusammensetzung AM^IC_2 typisch ionische Eigenschaften und nahezu den für eine Dreifachbindung erwarteten C–C-Abstand von 120 pm zeigen. Mit Hilfe einfacher chemischer Konzepte können diese Unterschiede aber plausibel gemacht werden. Ferner belegt der vorliegende Artikel, dass erst durch eine Kombination verschiedener Methoden (Pulverdiffraktion mit Röntgenstrahlung und Neutronen, Festkörper-NMR-Spektroskopie, Raman-Spektroskopie) diese neue Verbindungsklasse strukturell und chemisch charakterisiert werden konnte.

Introduction

Carbides are formed from combination of elemental carbon with other elements of lower electronegativity, mainly metals or semimetals. Therefore, compounds such as CO_2 , CS_2 , and, by convention, CH_4 are not regarded as carbides. The term “carbides” was first introduced in 1796 by de Fourcroy [1]. Depending on the differences in electronegativity of the constituents (ΔEN) three different classes of carbides may be distinguished [2].

If ΔEN is small, the bonding will be mainly covalent and these so-called *covalent carbides* show an extremely high hardness. SiC and B_4C are well-known examples for covalent carbides.

Metallic carbides have an intermediate ΔEN and metallic properties (e.g. metallic luster and conductivity), but this class is less well-defined. Therefore three subclasses are commonly introduced. In interstitial carbides transition metals, particularly of the IVth, Vth, and VIth Periodic Groups, form a close-packed structure with the carbon atoms occupying octahedral interstices. These carbides also show an extraordinary hardness and are chemically very robust. TiC , TaC , or MoC are examples for interstitial carbides crystallizing in the rocksalt structure type [3]. If the radius of the metal becomes smaller ($r_{\text{M}} < 130 \text{ pm}$), the octahedral holes are too small for accommodating carbon atoms ($r_{\text{C}}/r_{\text{M}} < 0.59$), which results in a distortion of the metal lattice. These carbides show an enhanced reactivity and a large variety of stoichiometries (Cr_7C_3 , Mn_5C_2 , or Fe_3C). The carbides of 4f and 5f elements should be considered separately, as they contain C_2 dumbbells [4]. Compounds of composition MC_2 (e.g. LaC_2 , ThC_2) and M_2C_3 (e.g. Pr_2C_3 , U_2C_3), better described as $\text{M}_4(\text{C}_2)_3$, are known.

Finally, for the highest ΔEN carbides with a salt-like behavior are found. As bonding is mainly ionic, they are called *ionic carbides*. Most of them are colorless and very sensitive to hydrolysis. Depending on the carbon anion different hydrocarbons are released upon hydrolysis. Methanides contain isolated carbon atoms (“ C^{4-} ” anions) and methane is released. Al_4C_3 and Be_2C are examples. In acetylides [5] C_2^{2-} anions are found and acetylene (ethyne) is released upon hydrolysis [6]. CaC_2 and Na_2C_2 are the most prominent members of this class. The only structurally characterized ionic carbide containing a C_3^{4-} anion is Mg_2C_3 . It releases a mixture of propyne and propadiene depending upon the conditions of hydrolysis. Alkali and alkaline-earth metal carbides have been reviewed very recently [7].

When we started our work on metal carbides in the 1990s we were mainly interested in ternary carbides consisting of an electropositive metal, in particular alkali metals, which usually form ionic carbides, and a transition metal usually forming a metallic carbide. We

were hoping that the properties of these novel compounds should be at the borderline between ionic and metallic behavior. By choosing the right elements and elemental ratios one could think of fine tuning the properties. Checking the literature at that time we found that no carbide of composition $A^I_xM_yC_z$ (A^I = alkali metal, M = transition metal) had structurally been characterized. Only the synthesis of $KAgC_2$ was described [8] and also some ternary alkaline-earth metal transition metal carbides (e.g. $Ca_4Ni_3C_5$ [9] and see chapter 3.2 in [7]) were known. But after starting our work in this field we first had to accept that many difficulties had to be overcome before a successful synthesis of a new alkali metal transition metal carbide was achieved. The typical synthesis of metal carbides is a high temperature synthesis by combining the elements or reacting metal oxides with carbon. We had to learn that the compounds we were looking for are thermally not stable so that new synthetic routes had to be developed. This research report shall give an overview about the results we have obtained within the last ten years in synthesizing new alkali metal transition metal acetylides [10].

But besides the preparative problems we had to face also characterization methods had to be developed or – as most of them had been known before – refined for our purposes. As the new ternary acetylides are synthesized by solid state reactions at low temperatures no single crystals can be obtained so that all structural solutions and refinements have to be based on powder diffraction data. Depending on the specific details of the crystal structure we used X-ray, neutron, or synchrotron radiation for our investigations. As acetylides contain C_2 dumbbells, which are symmetrically coordinated, IR spectroscopy cannot be used for characterizing C–C stretching vibrations, but Raman spectroscopy is best suited for this kind of investigations. In order to obtain data for comparison we synthesized many of the known binary acetylides and recorded their Raman spectra. Finally, ^{13}C MAS NMR spectroscopy turned out to be a very helpful method for characterizing binary and ternary acetylides even though we did not use ^{13}C enriched samples. Again, for comparison reasons, we synthesized and investigated many binary acetylides by ^{13}C MAS NMR spectroscopy. This research report will also give some details on the methods we used and how they helped us to get a deeper insight into this new class of compounds.

Compounds of Composition $A_2M^0C_2$ ($A = Na-Cs$; $M^0 = Pd, Pt$)

Synthesis. Na_2PdC_2 and Na_2PtC_2 were the first ternary alkali metal transition metal acetylides we were able to synthesize and characterize [11]. In an argon atmosphere Na_2C_2 is reacted with palladium or platinum sponge, which was prepared by reduction of $[Pd(NH_3)_2Cl_2]$ and $(NH_4)_2[PtCl_6]$ with H_2 prior to the synthesis.

The reaction starts at about 240°C, which is surprisingly low for a solid state reaction. It can be followed on a high temperature X-ray diffractometer (Figure 1) with the starting materials sealed in a glass capillary in an argon atmosphere.

< Figure 1 >

Therefore we examined the reaction of Na_2C_2 with palladium by in-situ X-ray powder diffraction to investigate the kinetics of this reaction. To decrease the time needed for recording a complete powder pattern these experiments were performed with synchrotron radiation (powder diffractometer at beamline B2, HASYLAB/DESY). Using a new detector system with an imaging plate (OBI [12]) the time needed for exposure and read out of a complete pattern was decreased to about five minutes. With this set-up the reaction of Na_2C_2 with palladium was investigated at five temperatures between 240 and 260°C [13]. Unfortunately, no reaction can be observed below 240°C, and above 260°C the reaction is too fast to be followed with the described set-up. All patterns were analyzed by Rietveld refinements to extract reliable molar ratios of the product in dependence of the reaction time. Based on the Avrami-Erofe'ev theory [14] the resulting crystallization curves were fitted to the equation $\alpha = 1 - e^{(-kt)^n}$ with α = reaction extent (i.e. molar ratio of the product), k = rate constant, and n = Avrami coefficient. The latter describes the mechanism of the reaction. A linearized form of this equation leads to Sharp-Hancock plots, which are shown in Figure 2. As we found that the reaction at the lowest temperature (240°C) cannot be described by the Avrami-Erofe'ev equation, it has been omitted in Figure 2. For the other temperatures an acceptable fit was obtained. From these fits an Avrami coefficient of approx. 0.3 was calculated for all temperatures, which is very small, but indicative for a diffusion controlled reaction. As expected the rate constant increases with increasing temperature and from an Arrhenius fit an activation energy $E_A = 480(120)$ kJ/mol resulted. This is in the range obtained for other solid state reactions, but the standard deviation is very high, and we are now trying to improve the set-up of our experiment to obtain more precise results.

< Figure 2 >

K_2PdC_2 and K_2PtC_2 were prepared from K_2C_2 and palladium/platinum sponge at similar conditions like the sodium compounds [15]. The synthesis of rubidium and cesium compounds led to some problems, as the starting materials Rb_2C_2 and Cs_2C_2 were not characterized completely. Their synthesis had been known for more than 100 years, however structural data were not available. As the knowledge of the crystal structure of a starting material is essential to check its purity and to be able to solve a new compound from powder diffraction data, we first had to solve the crystal structure of Rb_2C_2 and Cs_2C_2 . When we investigated these compounds, we found that both compounds are polymorphic coexisting in a hexagonal and an orthorhombic modification [16]. This, of course complicated the structural solution from powder diffraction data for a long time. But with the knowledge of the crystal structures of Rb_2C_2 and Cs_2C_2 the synthesis of $A_2M^0C_2$ ($A = Rb, Cs$; $M^0 = Pd, Pt$) and the solution and refinement of their crystal structures were straightforward [17].

Crystal Structures. All compounds of composition $A_2M^0C_2$ crystallize in isotypic crystal structures with hexagonal unit cells. The resulting lattice parameters are given in Table 1. From these parameters one can already guess the crystal structures, as the lattice constants c are almost independent of the respective alkali metal. Therefore a structural unit only consisting of palladium/platinum and carbon must run along $[001]$. This structural unit is a $\infty [M^0(C_2)_{2/2}^-]$ chain ($M^0 = Pd, Pt$) as can be seen in Figure 3. These chains are separated by the alkali metal ions.

< Table 1 >

< Figure 3 >

Palladium and platinum are linearly coordinated by two C_2 dumbbells in an end-on fashion, as commonly found for metals with a d^{10} configuration. Furthermore, both palladium/platinum atoms and C_2 dumbbells are coordinated octahedrally by six alkali metal ions. These octahedra are – especially around the C_2 units – distorted (see Figure 3). Somewhat surprising is the coordination around the alkali metal ions, as these sit in a distorted trigonal prism with three longer distances to the palladium/platinum atoms and three shorter distances to the carbon atoms. The expected side-on coordination of alkali metals by C_2 dumbbells is probably not realized due to repulsive interactions between two alkali metal ions. All crystal structures of ternary alkali metal palladium and platinum acetylides were solved and refined from X-ray powder diffraction data. To get more reliable interatomic distances additional neutron diffraction experiments were performed on Na_2PdC_2 and Na_2PtC_2 [15]. Most interestingly, the C–C distances are 126.3(3) and 128.9(4) pm. This is more than 6 pm longer than the expected

bond length for a C–C triple bond (120 pm). These interesting findings will be discussed later. Further interatomic distances for Na_2PdC_2 are given in Figure 3.

Another interesting aspect of Table 1 is a comparison of the lengths of the c axes, as the c axis in palladium compounds is by more than 5 pm longer than the c axis in the respective platinum compounds. This is probably a consequence of relativistic effects [18]. A similar effect is also found in ternary silver and gold acetylides, which will be discussed in the next chapter.

Properties. In our first experiments ternary palladium and platinum acetylides were obtained as black polycrystalline powders that are sensitive to air and moisture. But using a slightly modified synthesis – i.e. after a first reaction the product is ground and heated again – we obtained Na_2PdC_2 in form of a red powder [19]. Similar syntheses of the other ternary palladium and platinum acetylides are currently performed. From the color it can be presumed that these compounds are semiconductors, which is confirmed by temperature-dependent measurements of electrical conductivity [15]. But no linear behavior is found in $\ln(1/R) = f(1/T)$ plots (R = resistance) to calculate the band gap from these measurements. It must be assumed that two different conduction mechanisms exist. At lower temperatures the conduction is mainly affected by defects or impurities, whereas at higher temperatures the intrinsic conduction mechanism gains the upper hand. From an extrapolation to higher temperatures we estimated band gaps between 0.1 and 0.2 eV. These measurements were performed on black samples and it will be interesting to see, whether measurements on the newly synthesized red samples give different results.

< Figure 4 >

Nonetheless, the estimated band gaps are in good agreement with the band gaps obtained from band structure calculations using the LMTO (linear muffin-tin orbitals) method within density functional theory. The band structure and DOS curve for Na_2PdC_2 are shown in Figure 4. A small indirect band gap of approx. 0.2 eV and a larger direct band gap of approx. 2.6 eV can be read. The latter accounts for the red color of the sample. This is confirmed by measurements of diffuse reflectivity (Figure 5) on reddish Na_2PdC_2 [20]. In these measurements a direct band gap of approx. 2.2 eV, which corresponds to 576 nm, is obtained, again in reasonable agreement with the theoretical results. The good agreement between theoretical and experimental results is surprising, as LMTO calculations usually tend to underestimate band gaps. But here, the calculated band gaps are even larger than the experimental ones. For Na_2PtC_2 , on the other hand, a vanishing band gap is calculated, but our conductivity measurements show that Na_2PtC_2 is also a semiconductor like Na_2PdC_2 and

not a metal. Preliminary calculations using the WIEN2k code (full-potential augmented plane-wave and local orbitals method within density functional theory) reproduce the semiconducting behavior of Na_2PtC_2 correctly, but for Na_2PdC_2 band gaps are calculated, which differ even more from the experimental results. As already mentioned, we are currently optimizing the synthesis of ternary palladium and platinum acetylides to repeat the conductivity and diffuse reflectivity measurements on these samples. At the same time, highly accurate band structure calculations using the WIEN2k code shall be performed in an attempt to solve these discrepancies between theoretical and experimental results.

< Figure 5 >

Another interesting aspect of the band structure of Na_2PdC_2 is the large dispersion of the lowest conduction band between A and L (Figure 4), which is responsible for a small indirect and a larger direct band gap. Fat band analysis shows that this band is mainly a sodium band. Calculating the band structure of Na_2PdC_2 without sodium atoms leads to a smaller dispersion of this band and thus a larger indirect band gap. Therefore, interactions between sodium atoms and ${}^\infty[\text{Pd}(\text{C}_2)_{2/2}]$ chains must be assumed to be responsible for the remarkable electronic properties of Na_2PdC_2 . This assumption is supported by short Na–Pd distances in the crystal structure of Na_2PdC_2 (296.8(2) pm, see Figure 3). This Na–Pd distance is among the shortest found in the ICSD database [21]. A comparable distance between Na^+ and $\text{Pd}(0)$ was found in Na_2PdH_2 (300.0(1) pm) [22]. On powdered samples also semiconducting properties were measured and metal-metal interactions were assumed.

In order to characterize ternary palladium and platinum acetylides in more detail spectroscopic investigations have been performed. Especially ^{13}C solid-state MAS NMR spectroscopy has proven to be a powerful tool for further structural characterization, as for each distinct carbon site one set of resonance lines should be observed. The results of these investigations, which confirm the results of the structural investigations based on powder diffraction data, are summarized in Table 2. A static solid-state NMR spectrum of Na_2C_2 had been reported earlier [23], but for comparison reasons we also recorded ^{13}C MAS NMR spectra of Na_2C_2 and K_2C_2 [24]. It is found that the isotropic chemical shifts δ_{iso} are similar for binary and ternary acetylides, but they differ significantly from the shift found for acetylene [25]. A closer view reveals that the deshielding of binary acetylides is slightly larger than that of ternary palladium and platinum acetylides and increases as the number of electrons on the alkali metal rises. The latter effect is less pronounced for ternary acetylides. We also analyzed the intensities of spinning sidebands to determine the shielding parameters. These are also given in Table 2. For Na_2PtC_2 and K_2PtC_2 the poor quality of the spectra did

not allow a reliable analysis of spinning sidebands so that only isotropic chemical shifts are given. The shielding anisotropies $\Delta\sigma$ and asymmetry parameters η are discussed elsewhere [15]. In summary, ^{13}C NMR spectroscopy has turned out to be a very helpful tool for structural verification even at natural ^{13}C abundances.

< Table 2 >

Another useful method is Raman spectroscopy as stretching vibrations of C_2 dumbbells in acetylides cannot be observed in IR spectra due to the symmetric coordination of the dumbbells. Again, we have recorded Raman spectra of binary and ternary acetylides for a better comparison. These results are given in Table 4. They will be discussed later.

To summarize, compounds of composition $\text{A}_2\text{M}^0\text{C}_2$ ($\text{A} = \text{Na} - \text{Cs}$, $\text{M}^0 = \text{Pd}, \text{Pt}$) can be described in an ionic form according to $(\text{A}^+)_2\text{M}^0(\text{C}_2^{2-})$. In agreement with the d^{10} configuration of Pd^0 and Pt^0 a linear coordination is found and all compounds are diamagnetic as confirmed by temperature-dependent measurements of magnetic susceptibilities down to 1.7 K [26]. Interactions between alkali metal ions and palladium/platinum atoms due to short interatomic distances influence the electronic properties in a way that a semiconducting behavior results with very small indirect band gaps. Furthermore, C–C bond lengths significantly longer than those expected for a C–C triple bond are found. A reason for this will be given in the next chapter.

Compounds of Composition $AM^I C_2$ ($A = \text{Li-Cs}$; $M^I = \text{Cu, Ag, Au}$)

Synthesis. The synthesis of $KAgC_2$ was already reported in 1963 by Nast and Schindel [8]. They reacted KC_2H with highly explosive Ag_2C_2 in liquid ammonia:

By decreasing the $KC_2H:Ag_2C_2$ ratio almost pure $KAgC_2$ was obtained, which was only characterized by elemental analysis. As no signal for a C–C stretching vibration was found in IR spectra a symmetrical surrounding of C_2 dumbbells was concluded. To avoid the use of explosive Ag_2C_2 we modified the synthesis slightly:

Although the existence of $K[Ag(C_2H)_2]$ could not be proven by a structural characterization, as the compound is amorphous to X-rays, this intermediate is very likely, as the formation of KI and the evolution of a gas upon heating were found. The former can be removed with liquid ammonia so that single-phase $KAgC_2$ is obtained. Using this approach many ternary copper, silver, and gold acetylides were synthesized [27, 28, 29]. For the synthesis of some ternary copper acetylides a slightly different reaction route was used [27]:

This reaction is surprising, as A_2C_2 ($A = \text{K, Rb, Cs}$) was reported to be insoluble in liquid ammonia. As the reaction is very slow, we now assume that very small amounts of binary alkali metal acetylides are soluble in liquid ammonia so that the reaction can proceed in the liquid phase. Again after reaction alkali metal iodide can be removed with liquid ammonia and ternary copper acetylides are obtained in a pure form. To increase the crystallinity, heating of the samples to temperatures up to 470 K is necessary. A list of all ternary copper, silver, and gold acetylides we were able to synthesize is given in Table 3. Copper and silver compounds are colorless to slightly gray – probably due to small amounts of carbon containing decomposition products –, whereas gold compounds are yellow.

Crystal Structures. Again no single crystals could be obtained and all crystal structures had to be solved and refined from powder diffraction data. The resulting unit cells are given in Table 3. Like in ternary palladium and platinum acetylides small unit cells were found, but here three different structure types are observed. The crystal structure of $KAgC_2$ [28] is shown in Figure 6. ${}^\infty[Ag(C_2)_{2/2}]^-$ chains parallel to $[001]$ are separated by potassium ions. Each

potassium ion is surrounded side-on by four C_2 dumbbells. Their centers of gravity form a square planar coordination sphere around each K^+ (Figure 6). The C_2 units reside inside distorted octahedra formed by four potassium ions and two silver ions in trans positions. Based on neutron powder diffraction data a C–C distance of 122.3(6) pm was determined. This is closer to the expected bond length for a C–C triple bond (120 pm) than the C–C distances found in ternary palladium and platinum acetylides. The shortest K–Ag distance is 399.0(1) pm (8 x). More interatomic distances are given in Figure 6.

< Table 3 >

< Figure 6 >

The crystal structure of $LiAgC_2$ [28] is shown in Figure 7. Again ${}^1_{\infty}[Ag(C_2)_{2/2}]^-$ chains parallel to [001] are the characteristic structural units, which are separated by lithium ions. Each lithium ion is surrounded side-on by three C_2 dumbbells. The C_2 units reside inside a distorted trigonal bipyramid formed by three lithium ions and two silver ions in axial positions (Figure 7). Based on neutron powder diffraction data a C–C distance of 127.8(6) pm was determined. This is much longer than the expected bond length of 120 pm for a C–C triple bond, but it was assumed that this value is an artifact due to problems in the Rietveld refinement caused by impurities and anisotropic reflection broadening (Figure 12). More interatomic distances are given in Figure 7.

< Figure 7 >

The crystal structure of $CsAgC_2$ [28] is shown in Figure 8. Again ${}^1_{\infty}[Ag(C_2)_{2/2}]^-$ chains are the characteristic structural units, but here they are aligned in layers perpendicular to [001]. These layers are rotated by 90° to each other such that a stacking ABAB... results. The cesium ions are located between these layers. Each of them is surrounded side-on by four C_2 dumbbells. Their centers of gravity form a tetrahedral coordination sphere around each Cs^+ (Figure 8; compare to $KAgC_2$ with a square planar coordination, Figure 6). The C_2 units reside in distorted octahedra formed by four cesium ions and two silver ions in trans positions. Based on neutron powder diffraction data a C–C distance of 121.7(7) pm was determined. This is close to the expected bond length of 120 pm for a C–C triple bond. The shortest Cs–Ag distance is 427.9(1) pm (8 x). More interatomic distances are given in Figure 8.

< Figure 8 >

The crystal structures of $LiAgC_2$, $KAgC_2$, and $CsAgC_2$ represent the most simple examples for rod packings as given by O’Keeffe and Andersson [30] considering the ${}^1_{\infty}[Ag(C_2)_{2/2}]^-$

chains as rods. LiAgC_2 represents a simple hexagonal rod packing, whereas KAgC_2 and CsAgC_2 are examples for two types of simple tetragonal rod packings. All ternary alkali metal acetylides $\text{AM}^{\text{I}}\text{C}_2$ (A = alkali metal, $\text{M}^{\text{I}} = \text{Cu, Ag, Au}$) we were able to synthesize within the last years crystallize in one of these three structure types. This is summarized in Figure 9 and Table 3. In two cases a dimorphic behavior was found. RbCuC_2 and CsAgC_2 crystallize in the KAgC_2 and the CsAgC_2 structure type. No phase transition between the two polymorphs was observed and it is unclear which of them is the thermodynamic stable modification, but in both cases the one in the KAgC_2 structure type has the higher density.

< Figure 9 >

The stability of the different structure types can be understood based on a very simple model of close-packed rods with spheres – i.e. alkali metal ions – occupying the interstitial holes in-between. This model, which calculates the space filling of the different structure types in dependence of $r(\text{S})/r(\text{R})$ ($r(\text{S})$ = radius sphere, i.e. alkali metal ion; $r(\text{R})$ = radius rod, i.e. $[\text{M}^{\text{I}}(\text{C}_2)_{2/2}]^-$ chain), has already been described elsewhere [29].

An interesting aspect of Table 3 is a comparison of lattice parameters of ternary silver and gold acetylides in LiAgC_2 and KAgC_2 structure types. It is obvious that the lattice parameter c , which is the sum of two $\text{M}^{\text{I}}\text{--C}$ bonds and one C--C bond ($\text{M}^{\text{I}} = \text{Ag, Au}$) and thus almost independent on the respective alkali metal, is by more than 10 pm longer in the silver compounds compared to the respective gold compounds. Like the already discussed similar findings in ternary palladium and platinum acetylides, this can be attributed to relativistic effects [18]. For ternary palladium/platinum acetylides the differences of lattice parameters c are smaller (approx. 5 pm) than for ternary silver/gold acetylides (approx. 10 pm). It was predicted that relativistic effects should have the most important influence for the pair Ag-Au [18].

Properties. As already mentioned ternary copper and silver acetylides of composition $\text{AM}^{\text{I}}\text{C}_2$ are colorless to slightly gray. The respective gold compounds are yellow, their colors darken slightly from the lithium to the cesium compound. The band structure and DOS curve for CsAgC_2 (LMTO method within density functional theory) are shown in Figure 10. The smallest band gap is the direct band gap of approx. 2.3 eV. As already mentioned, calculations based on the LMTO method usually tend to underestimate band gaps. Therefore this band structure is in good agreement with an insulating behavior of CsAgC_2 , which was found in measurements of electrical conductivity.

< Figure 10 >

For ternary palladium and platinum acetylides we showed that solid-state NMR spectroscopy is a very helpful tool to get a more detailed view on the structural properties of these compounds. For ternary copper, silver and gold acetylides ^{13}C solid-state NMR spectra have only been recorded for KCuC_2 , RbCuC_2 and CsCuC_2 up to now [27]. But for those we measured very interesting spectra (Figure 11), as the carbon resonance line is complicatedly split due to coupling of the carbon nucleus ($I = 1/2$) with the copper nuclei ($I = 3/2$ for the isotopes ^{63}Cu and ^{65}Cu). Additionally, the dipolar interaction between the copper nuclei has to be considered. Only a few examples of these effects in ^{13}C –Cu pairs have been seen before [31, 32]. As obvious from Figure 11 the deshielding increases with an increasing number of electrons of the alkali metal. The same observation was made for binary alkali metal and ternary palladium and platinum acetylides (Table 2). The Raman spectroscopic properties of ternary copper, silver and gold acetylides will be discussed together with the Raman spectroscopic results on ternary palladium and platinum acetylides in the next chapter.

< Figure 11 >

Looking at Table 3 it is notable that the standard deviations of the lattice parameters of ternary gold acetylides are very high. This is due to a bad crystallinity and a severe anisotropic peak broadening, which was found in all compounds crystallizing in the LiAgC_2 or KAgC_2 structure types, but the strongest effect was found for the gold acetylides. The latter effect was also given as an explanation for the problems in refining neutron powder diffraction data of LiAgC_2 . To visualize the strength of this effect a small range of the X-ray powder diffraction pattern of LiAgC_2 is shown in Figure 12. Even with the profile functions included in typical Rietveld refinement programs a proper handling of this effect is not always possible. The anisotropic peak broadening seems to display the anisotropic structural features of compounds crystallizing in LiAgC_2 or KAgC_2 structure types, where all transition metal carbon chains are running parallel to each other along to the c axis. (00l) reflections are therefore sharp, whereas all other reflections are severely broadened. On the other hand, compounds crystallizing in the CsAgC_2 structure type, where the chains are not running parallel to one axis, do not show this effect.

< Figure 12 >

Comparison of properties: Na₂PdC₂ vs. CsAgC₂

For Na₂PdC₂ Na–Pd interactions have been discussed in one of the last chapters, which lead to a small indirect band gap and semiconducting behavior. These interactions are probably a consequence of short Na–Pd distances (Na–Pd: 296.8 pm) in the crystal structure of Na₂PdC₂, which are among the shortest Na–Pd distances found in the ICSD database. For Cs₂PdC₂ [17], which is also a semiconductor, Cs–Pd distances of 355.6 pm have been determined, which are also among the shortest Cs–Pd distances found in this database. Compared to this the shortest Cs–Ag distances in CsAgC₂ (427.9 pm) and Na–Ag distances in NaAgC₂ (375.4 pm) [28] are not remarkable and Cs–Ag/Na–Ag interactions can be excluded. Accordingly, no large dispersions of the conduction bands and no small indirect band gaps are found (compare Figure 4 and Figure 10). Thus, the different electronic properties of ternary silver and palladium acetylides can be put down to slight differences in their crystal structures. In compounds of composition AAg^IC₂ there is only one alkali metal cation per formula unit needed to compensate the charge of $\frac{1}{\infty}[\text{Ag}(\text{C}_2)^{-}_{2/2}]$ chains. This cation occupies a position side-on to C₂²⁻ dumbbells. However, in compounds of composition A₂Pd⁰C₂ two alkali metal cations per formula unit are needed for charge compensation. Due to coulomb repulsion two alkali metal cations can no longer coordinate the C₂²⁻ dumbbells side-on and they are shifted towards the palladium atoms. Thus, shorter A–Pd distances result, which lead to interactions with the consequences discussed above. To support this model we are trying to synthesize MgPdC₂ or other alkaline-earth metal palladium acetylides. If they crystallize in crystal structures isotopic to ternary silver acetylides of composition AM^IC₂, it will be interesting to measure their electronic properties. According to the model discussed above they should be insulators, as no A^{II}–Pd interactions should occur (A^{II} = Mg–Ba). Unfortunately, all our attempts to synthesize these compounds have not been successful up to now. The discussion has been restricted to silver and palladium acetylides, as more information about their properties is available, but, of course, ternary platinum and gold acetylides can also be included in this model.

As already mentioned Raman spectra were recorded on all ternary acetylides we were able to synthesize within the last years. We were mainly interested in the frequencies of C–C stretching vibrations, as they are good indicators for the electronic properties within the C₂ dumbbells and thus within the whole metal-carbon chain. For comparison also spectra of binary alkali metal acetylides were recorded. These results are summarized in Table 4. In a few spectra of very high quality also signals for metal-carbon vibrations are visible at low

frequencies. But as they are not visible in all spectra a comparing discussion is not possible and therefore these results will not be given here.

< Table 4 >

Several aspects of the wave numbers given in Table 4 need to be commented or discussed. First, there is a nice agreement between the results of ^{13}C solid-state NMR experiments (Table 2) and Raman spectroscopy with respect to the differences between C_2H_2 and binary acetylides. Like the isotropic chemical shift in NMR experiments also the stretching frequency of the C–C bond differs by more than 100 cm^{-1} for C_2H_2 and binary acetylides. Furthermore, the deshielding of binary acetylides, which increases with an increasing number of electrons of the alkali metal, parallels with the C–C stretching frequencies, which decrease with the electron count of the alkali metal. This can be interpreted by decreasing electronegativity of the alkali metal, which increases the negative charge in the C_2 unit. Similar trends in both NMR and Raman spectra are found for ternary palladium, platinum and copper acetylides, but here the trend is less pronounced. One can suspect that this is due to the covalency within the metal-carbon chains so that the influence of ionic interactions by the alkali metals is smaller. For ternary silver and gold acetylides no influence of the alkali metal is found at all. Comparing ternary acetylides, the C–C stretching vibrations decrease from palladium to platinum compounds, whereas from copper to silver to gold acetylides they increase. The latter parallels nicely the findings for ternary cyanides [35, 36]. But the most intriguing aspect of Table 4 is a comparison of the wave numbers of ternary palladium and silver acetylides with isoelectronic metal-carbon chains [37]. There is a difference of more than 100 cm^{-1} , which needs to be explained. In Table 5 some properties and structural data of Na_2PdC_2 and CsAgC_2 are summarized, for which most data are available and which are good model compounds for the whole series. It is obvious that there are several differences, although both compounds have isoelectronic metal-carbon chains.

< Table 5 >

An explanation for the different colors and electronic properties has already been given. The different C–C bond lengths are in good agreement with the wave numbers of the C–C stretching vibrations, although a direct correlation between bond length and frequency of the vibration has always to be considered with some care. But in most cases the bond weakens with an increasing bond length and the frequency of its vibration decreases. This is found comparing CsAgC_2 and Na_2PdC_2 . Surprisingly, the Ag–C bond length in CsAgC_2 is longer than the Pd–C bond length in Na_2PdC_2 , although Ag^+ is smaller than Pd^0 . This leads to the following explanation using well-known chemical concepts. Back bonding from palladium

into the antibonding orbitals of the C₂ unit increases the C–C bond length compared to a C–C triple bond. For CsAgC₂ back bonding is less pronounced and the C–C bond length is closer to the expected bond length of a C–C triple bond (120 pm). On the other hand, the back bonding strengthens and shortens the M–C bond, which is also found for Na₂PdC₂. This is best described by the following Lewis electron-dot diagrams:

(1)

(2)

The bonding situation in CsAgC₂ is more or less described by diagram (1), whereas for Na₂PdC₂ also diagram (2) has to be taken into account. This simple model, which is well-known from many carbonyl complexes, is confirmed by analysis of the band structures shown in Figure 4 and 10. The COHPs (crystal orbital Hamilton populations) of the π -M–C bonding – mainly consisting of overlaps of the metal d- π orbitals with carbon p- π orbitals – can be extracted and compared for Na₂PdC₂ and CsAgC₂. Already a visual inspection (not shown here) confirms the stronger back bonding in Na₂PdC₂. In Table 5 the integrated values (iCOHP) are given. A higher iCOHP for Na₂PdC₂ indicates a stronger back bonding in this compound.

Another experiment to confirm the different electronic properties of Na₂PdC₂ and CsAgC₂ would be the hydrolysis. As already mentioned [6], metallic carbides release a complex mixture of hydrocarbons and hydrogen upon hydrolysis, whereas for ionic carbides only one hydrocarbon corresponding to the respective carbon anion (CH₄, C₂H₂ or C₃H₄) is released. Our first experiments seem to confirm these expectations, as for KAgC₂ only C₂H₂ and for Na₂PdC₂ C₂H₂ and C₂H₆ are detected. Unfortunately, with the set-up we used neither hydrogen nor C₂H₄ can be detected, so that further experiments on different instruments are needed to confirm these findings.

To summarize, despite their structural similarities Na₂PdC₂ and CsAgC₂ have many different properties, but most of these differences can be explained based on simple and illustrative models. Thus, because of their structural simplicity, Na₂PdC₂ and CsAgC₂ are good model compounds for scrutinizing these chemical concepts.

NaCu₅(C₂)₃ [38]

During the synthesis of NaCuC₂ we observed several color changes, while heating the residue of the reaction in liquid ammonia. The precipitate of the reaction of NaC₂H with CuI (Na:Cu = 2:1) in liquid ammonia is red, but after heating this precipitate a yellow color is observed (dynamic vacuum, 30 min, 463 K). After removal of NaI by extraction with liquid ammonia an orange product is obtained, which, after its structural characterization based on X-ray powder diffraction data, turned out to be NaCu₅(C₂)₃. By heating the red residue of the synthesis in liquid ammonia with longer heating rates (> 30 min) almost colorless NaCuC₂ is obtained. This reaction sequence is surprising, as products with different Na:Cu ratios are obtained and no extra reflections are found in the diffraction patterns. But the observation of a high background in the diffraction pattern of NaCu₅(C₂)₃ points to amorphous impurities, which probably contain sodium. Surprisingly, attempts to synthesize NaCu₅(C₂)₃ using the stoichiometric ratio (Na:Cu = 6:5) according to the following reaction scheme were not successful:

But despite its somewhat obscure synthesis NaCu₅(C₂)₃ is an interesting compound, as it is the first example of a ternary alkali metal transition metal acetylide with a three dimensional framework structure formed by Cu^I ions and C₂²⁻ dumbbells (Figure 13). Small channels parallel to [100] and [001] are found. At the intersections of these channels the sodium ions reside. Short Cu^I–Cu^I distances starting at 244 pm are another characteristic structural feature of this compound. The crystal structure of NaCu₅(C₂)₃ contains three distinct copper sites, three carbon sites and one sodium site. Not all structural details shall be discussed here and it is referred to the literature [38]. As sodium ions reside at the intersection of two small channels we tried to exchange sodium by other alkali metal ions using typical solution based ion exchange techniques. For the resulting solid of lithium exchange we found a similar diffraction pattern with slightly shifted reflections compared to the pattern of NaCu₅(C₂)₃, but large reflection widths hampered a structural solution up to now.

< Figure 13 >

The composition of NaCu₅(C₂)₃ is very close to copper acetylide Cu₂C₂ ≡ CuCu₅(C₂)₃, whose crystal structure is still unknown, as it is only obtained in amorphous forms. A possible structural relationship between NaCu₅(C₂)₃ and Cu₂C₂ was tested by comparing their IR and Raman spectra [38]. But as there are big differences in the IR spectra it is very unlikely that

$\text{NaCu}_5(\text{C}_2)_3$ represents a crystalline model compound for the unknown crystal structure of Cu_2C_2 .

Outlook

One of the most important aims of our current research in the field of ternary alkali metal transition metal acetylides is the extension of to transition metals, where two or three dimensional polyanions can be expected. An approach, which is similar to the successful synthesis of ternary copper, silver and gold acetylides, uses ethynylometallates as precursors according to

with A = alkali metal and M^y = transition metal in oxidation state y . In this respect, ethynylzincates, -cadmates, -cuprates, -manganates, and -nickelates have caught our special attention. Many of them have already been synthesized [39], but only in very rare cases structural data are available [40]. Furthermore some of them are very shock sensitive and tend to explode heavily. As tetraethynylzincates and -cadmates were not reported to be explosive, we have first concentrated on these compounds. The syntheses [41, 42] and the crystal structures of $K_2[M^{II}(C_2H)_4]$ with $M^{II} = Zn, Cd$ [40] had already been reported. We were able to extend the syntheses to the respective sodium, rubidium and cesium compounds [43]. Most of them are isotypic to $K_2[Zn(C_2H)_4]$ [40]. As an example the crystal structure of $Cs_2[Cd(C_2H)_4]$ is shown in Figure 14. Due to strong absorption of $CuK\alpha_1$ radiation it was refined on the basis of synchrotron powder diffraction data ($\lambda = 70.878$ pm).

< Figure 14 >

The crystal structure is characterized by isolated $[Cd(C_2H)_4]^{2-}$ tetrahedra. It shows some similarities to the scheelite structure ($CaWO_4$). Both sodium compounds are amorphous to X-rays, but from their spectroscopic data (Table 6) it can be concluded that they also consist of $[M^{II}(C_2H)_4]^{2-}$ tetrahedra ($M^{II} = Zn, Cd$). $Cs_2[Zn(C_2H)_4]$ gives a powder pattern with sharp reflections, but we have not been able to solve its crystal structure up to now, as no successful indexation of the powder pattern could be performed. The spectroscopic data show that it should also contain $[Zn(C_2H)_4]^{2-}$ tetrahedra, but the slight differences in the wave numbers compared to other compounds confirm that it is possibly not isotypic to $K_2[Zn(C_2H)_4]$. All compounds of composition $A^{II}[M^{II}(C_2H)_4]$ ($A^{II} = Mg - Ba$; $M^{II} = Zn, Cd$) are amorphous to X-rays, but from their Raman spectra the existence of $[M^{II}(C_2H)_4]^{2-}$ tetrahedra can also be concluded [43].

< Table 6 >

When crystallizing $K_2[Zn(C_2H)_4]$ from liquid ammonia at low temperatures we found that colorless transparent single crystals are obtained, which keep their well-defined habit at room

temperature. But they become dull and their diffraction patterns only show Debye rings on an X-ray single crystal diffractometer. Measurements at low temperatures revealed that an ammoniate of composition $\text{K}_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 2 \text{NH}_3$ forms [44], which loses its ammonia with raising temperature to give $\text{K}_2[\text{Zn}(\text{C}_2\text{H})_4]$. An ORTEP diagram of the molecular structure of the ammoniate is shown in Figure 15. Apart from the expected $[\text{Zn}(\text{C}_2\text{H})_4]^{2-}$ tetrahedron two crystallographically distinct potassium ions are found. One is solely coordinated side-on by six C_2H^- groups, whereas the other is coordinated side-on by four C_2H^- groups and two ammonia molecules. Single crystals of an isotopic cadmium compound were also obtained [44]. Also single crystals of an analogous manganese compound were synthesized, but due to their high thermal instability and sensitivity it was not possible to measure one of them on an X-ray powder diffractometer up to now.

< Figure 15 >

In similar experiments we were able to crystallize ammoniates with the composition $\text{Ca}[\text{Cu}(\text{C}_2\text{H})_3] \cdot 6 \text{NH}_3$ and $\text{Rb}_2[\text{Cu}(\text{C}_2\text{H})_3] \cdot \text{NH}_3$ [45]. Here, no single crystals could be obtained, but it was possible to isolate a well crystallized powder suitable for X-ray powder investigations, if all handling was carried out in an ammonia atmosphere including the sealing of the capillaries. Loosing the ammonia leads to amorphous compounds with a color change from colorless to yellow. The crystal structures of the ammoniates however were solved and refined from X-ray powder diffraction data [45]. They contain the unusual trigonal planar $\text{Cu}(\text{C}_2\text{H})_3^{2-}$ anion. The crystal structure of $\text{Ca}[\text{Cu}(\text{C}_2\text{H})_3] \cdot 6 \text{NH}_3$ is shown in Figure 16, which can be described as an arrangement of $[\text{Ca}(\text{NH}_3)_6]^{2+}$ cations and $\text{Cu}(\text{C}_2\text{H})_3^{2-}$ anions similar to hexagonal BN. The crystal structures of $\text{Rb}_2[\text{Cu}(\text{C}_2\text{H})_3] \cdot \text{NH}_3$ and isotopic $\text{Cs}_2[\text{Cu}(\text{C}_2\text{H})_3] \cdot \text{NH}_3$, which is even more sensitive and was not obtained in a pure form, are more complicated [45] and will not be shown here. It was possible to measure the Raman spectra of these ammoniates. The results are included in Table 6. However, $\text{K}_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 2 \text{NH}_3$ and $\text{K}_2[\text{Cd}(\text{C}_2\text{H})_4] \cdot 2 \text{NH}_3$ are thermally so sensitive that their Raman spectra could not be recorded.

< Figure 16 >

Following our observations it was possible to synthesize and characterize new and interesting ammoniates of ethynylometallates. But coming back to the idea of the beginning of this chapter it was not possible up to now to convert these ethynylometallates into ternary alkali metal transition metal acetylides. In none of our experiments we were able to obtain well crystallized powders. Also experiments under ammonothermal conditions only resulted in

powders amorphous to X-rays. In current experiments we are trying to improve the conditions for crystallization by changing temperature, pressure and/or solvent.

Another interesting approach is the replacement of C_2^{2-} dumbbells by other linear carbon rich anions, i.e. $C\equiv C-C\equiv C^-$ or $C\equiv C-C_6H_4-C\equiv C^-$. Here, our investigations are just in the beginning, but replacing C_2H^- by $C\equiv C-CH_3$ has already led to some new and interesting compounds of silver and copper. The crystal structures of $Ag(C_3H_3) \equiv Ag[Ag(C_3H_3)_2]$ and $Na[Ag(C_3H_3)_2]$ [46], again solved and refined from X-ray powder diffraction data, are shown in Figure 17. Both structures are surprising, as bent $Ag(C_3H_3)_2^-$ units are found. Furthermore, both compounds are isotypic with sodium ions replacing one half of the silver atoms in $Ag(C_3H_3)$. To confirm these results ^{109}Ag CP MAS solid state NMR spectra were recorded. As expected one isotropic signal was found for $Na[Ag(C_3H_3)_2]$, whereas two isotropic signals were found for the two distinct silver sites in $Ag(C_3H_3)$. Additionally, a strong SHG signal was measured for $Na[Ag(C_3H_3)_2]$, which confirms the acentric space group $Amm2$. A SHG signal of $Ag(C_3H_3)$ could not be measured, as the sample decomposed in the laser beam.

< Figure 17 >

The crystal structure of $Cu(C_3H_3)$, which was also solved and refined from X-ray powder diffraction data, is shown in Figure 18. It shows one-dimensional chains with short Cu–Cu distances [46]. The large variety of structural arrangements of compounds with the $C_3H_3^-$ anion is also exemplified by the crystal structure of $Rb[Ag(C_3H_3)_2]$, which is shown in Figure 19. Here $^\infty[Ag(C_3H_3)_2]^-$ helices parallel to the hexagonal c axis are found [47].

< Figure 18 >

< Figure 19 >

The interest in homoleptic aryl/alkylethynyl complexes is documented by a recent publication on such compounds consisting of $RC\equiv C^-$ ($R = tBu, nPr, Ph$) and M^+ ($M = Cu, Ag, Au$) [48] and a recent review [49]. In the past results in this field have mainly been hampered by the fact that no single crystals were available. But with improvements in collection and analysis of powder diffraction data the crystal structures of many more ethynylometallates will be solved in the near future, if a well-crystallized powder can be obtained. But even this is sometimes a problem as obvious from our work and the results in [48]. Thus, the conditions for crystallization have to be fine tuned, which needs a lot of chemical intuition. But the combination of chemical and crystallographic know-how needed in this field is of great appeal for us.

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Figure Captions

Fig. 1 Formation of Na_2PdC_2 from Na_2C_2 and palladium with increasing temperature as measured on an X-ray powder diffractometer (Huber G644, $\text{CuK}\alpha_1$ radiation). The reflection assignments and the starting temperature of the reaction are highlighted.

Fig. 2 Sharp-Hancock plots as obtained from isothermal in-situ X-ray powder investigations (HASYLAB, beamline B2) on the formation of Na_2PdC_2 from Na_2C_2 and palladium.

Fig. 3 Crystal structure of Na_2PdC_2 ($\text{P}\bar{3}\text{m1}$, $Z = 1$). Selected interatomic distances are: Pd–C 200.2(2) pm, Na–Pd 296.8(2) pm, Na–C 263.1(1) pm, C–C 126.3(3) pm.

Fig. 4 Band structure and DOS curve (LMTO) for Na_2PdC_2 . The Fermi level is indicated.

Fig. 5 Diffuse reflectivity of Na_2PdC_2 depending on the radiation wavelength. The band gap is marked.

Fig. 6 Crystal structure of KAgC_2 ($\text{P4}/\text{mmm}$, $Z = 1$). Selected interatomic distances are: Ag–C 203.2(3) pm, K–Ag 399.0(1) pm, K–C 305.1(1) pm, C–C 122.3(6) pm.

Fig. 7 Crystal structure of LiAgC_2 ($\text{P}\bar{6}\text{m2}$, $Z = 1$). Selected interatomic distances are: Ag–C 202.5(3) pm, Li–Ag 344.7(2) pm, Li–C 227.9(1) pm, C–C 127.8(6) pm.

Fig. 8 Crystal structure of CsAgC_2 ($\text{P4}_2/\text{mmc}$, $Z = 2$). Selected interatomic distances are: Ag–C 201.5(4) pm, Cs–Ag 427.9(1) pm, Cs–C 343.5(1) pm, C–C 121.7(7) pm.

Fig. 9 The crystal structures of ternary acetylides of composition $\text{AM}^{\text{I}}\text{C}_2$ ($\text{A} = \text{alkali metal}$, $\text{M}^{\text{I}} = \text{Cu, Ag, Au}$) can be described as simple rod packings as given by O’Keeffe and Andersson [30].

Fig. 10 Band structure and DOS curve (LMTO) for CsAgC₂. The Fermi level is indicated.

Fig. 11 ¹³C MAS NMR spectra of KCuC₂, RbCuC₂, and CsCuC₂ (Bruker Avance DSX500; ¹³C frequency: 125.841 MHz; spinning rate: 5 kHz; recycle delay: 30 s; number of scans: 7968, 7776, and 3264 for KCuC₂, RbCuC₂, and CsCuC₂, respectively). Spinning sideband intensities are added up to the isotropic signal.

Fig. 12 LiAgC₂: detail of X-ray powder diffraction pattern (Stoe Stadi P, CuKα₁ radiation) highlighting strong anisotropic broadening of reflection profiles typical for this class of compounds.

Fig. 13 Crystal structure of NaCu₅(C₂)₃ (Pnma, Z = 4): projections along [100] (top) and [001] (bottom).

Fig. 14 Crystal structure of Cs₂Cd(C₂H)₄ (I4₁/a, Z = 4).

Fig. 15 Ortep diagram of the molecular structure of K₂Zn(C₂H)₄ · 2 NH₃ (I2/a, Z = 4) showing 50% probability thermal ellipsoids and the atom-numbering scheme.

Fig. 16 Crystal structure of CaCu(C₂H)₃ · 6 NH₃ (P6₃mc, Z = 2). Hydrogen atoms have been omitted.

Fig. 17 Crystal structure of a) Ag(C₃H₃) (Amm2, Z = 4) and b) NaAg(C₃H₃)₂ (Amm2, Z = 2). Hydrogen atoms have been omitted.

Fig. 18 Crystal structure of Cu(C₃H₃) (P2₁/c, Z = 4). Hydrogen atoms have been omitted.

Fig. 19 Crystal structure of $\text{RbAg}(\text{C}_3\text{H}_3)_2$ ($R\bar{3}$, $Z = 18$) in a projection approx. along $[001]$ (left). The helical $^1_\infty[\text{Ag}(\text{C}_3\text{H}_3)_2]^-$ polyanion is shown on the right. Hydrogen atoms have been omitted.

Table 1 Lattice parameters of ternary alkali metal transition metal acetylides of composition $A_2M^0C_2$ ($A = Na-Cs$; $M^0 = Pd, Pt$) [15, 17].

Compound	a/pm	c/pm	V/nm ³
Na ₂ PdC ₂	446.38(1)	526.68(2)	0.090883(7)
K ₂ PdC ₂	510.33(2)	528.28(2)	0.119150(9)
Rb ₂ PdC ₂	535.81(2)	528.88(3)	0.13149(1)
Cs ₂ PdC ₂	562.36(2)	529.76(2)	0.14509(1)
Na ₂ PtC ₂	450.31(3)	520.50(5)	0.09140(1)
K ₂ PtC ₂	512.18(1)	521.79(1)	0.118539(7)
Rb ₂ PtC ₂	536.88(2)	522.45(2)	0.13041(1)
Cs ₂ PtC ₂	563.01(2)	522.94(3)	0.14355(1)

Table 2 ^{13}C Solid-state MAS NMR data of ternary alkali metal transition metal acetylides of composition A_2MC_2 [15]. Results on Na_2C_2 , K_2C_2 [24], and C_2H_2 [25] are given for comparison.

Compound	$\delta_{\text{iso}}/\text{ppm}^{[\text{a}]}$	$\Delta\sigma/\text{ppm}^{[\text{b}]}$	$\eta^{[\text{c}]}$
Na_2PdC_2	157	359	0.20
Na_2PtC_2	156	--- ^[d]	--- ^[d]
K_2PdC_2	162	317	0.15
K_2PtC_2	162	--- ^[d]	--- ^[d]
Na_2C_2	172	342	0.17
K_2C_2	186	285	0.15
$\text{C}_2\text{H}_2^{[\text{e}]}$	70	240	0

^[a] relative to external tetramethylsilane (TMS)

$$\delta_{\text{iso}} = -\sigma_{\text{iso}} = -1/3 \cdot (\sigma_{11} + \sigma_{22} + \sigma_{33}); \quad |\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}|$$

^[b] anisotropy: $\Delta\sigma = \sigma_{33} - 1/2 \cdot (\sigma_{11} + \sigma_{22})$

^[c] asymmetry: $\eta = 3/2 \cdot (\sigma_{22} - \sigma_{11})/\Delta\sigma$

^[d] not determined

^[e] static measurement with cross polarization

Table 3 Structural data of ternary alkali metal transition metal acetylides of composition $AM^I C_2$ (A = Li-Cs; M^I = Cu [27], Ag [28], Au [29]).

compound	a/pm	c/pm	V/nm ³	structure type
NaCuC ₂	376.61(2)	495.95(2)	0.070343(9)	KAgC ₂
KCuC ₂	490.79(3)	762.23(6)	0.18360(3)	CsAgC ₂
RbCuC ₂	491.79(8)	832.6(1)	0.20137(9)	CsAgC ₂
	446.5(1)	492.5(2)	0.09816(6)	KAgC ₂
CsCuC ₂	494.06(4)	914.2(1)	0.22314(6)	CsAgC ₂
LiAgC ₂	378.82(5)	532.8(3)	0.06621(4)	LiAgC ₂
NaAgC ₂	374.7(1)	532.0(1)	0.07469(6)	KAgC ₂
KAgC ₂	422.67(8)	528.7(2)	0.09445(6)	KAgC ₂
RbAgC ₂	447.5(1)	531.0(1)	0.10634(6)	KAgC ₂
CsAgC ₂	524.67(6)	852.8(1)	0.23474(7)	CsAgC ₂
	471.49(8)	525.9(3)	0.1169(1)	KAgC ₂
LiAuC ₂	378.7(5)	519.4(7)	0.0645(3)	LiAgC ₂
NaAuC ₂	373.0(8)	520(2)	0.0723(5)	KAgC ₂
KAuC ₂	418.4(8)	516(2)	0.0903(6)	KAgC ₂
RbAuC ₂	422(2)	519(1)	0.0922(8)	KAgC ₂
CsAuC ₂	461(1)	519(1)	0.1101(8)	KAgC ₂

Table 4 Raman spectroscopy: wave numbers [cm^{-1}] of C–C stretching vibrations ($\tilde{\nu}(\text{C}\equiv\text{C})$) of binary and ternary alkali metal acetylides and acetylene.

	A_2C_2	A_2PdC_2	A_2PtC_2	ACuC_2 [27]	AAgC_2 [28]	AAuC_2 [29]
A = H	1974 [33]					
A = Li	1872 [34]				1962	1998
A = Na	1845 [24]	1862 [15]	1845 [15]		1965	1997
A = K	1821 [24]	1850 [15]	1840 [15]	1959	1963	1997
A = Rb	1807 [16] ^[a]	1842 [17]	1833 [17]	1949	1961	1991
A = Cs	1796 [16] ^[a]	1841 [17]	1835 [17]	1945	1965	1993

^[a] Orthorhombic modification (Pnma, Z = 4)

Table 5 Comparison of properties and structural data of Na₂PdC₂ and CsAgC₂.

	Na ₂ PdC ₂	CsAgC ₂
Color	red	colorless
Electronic property	semiconductor	insulator
C–C/pm	126.4(3)	121.7(7)
M–C/pm	200.1(1)	201.5(4)
$\tilde{\nu}$ (C $\equiv$ C)/cm ^{−1}	1862	1965
iCOHP (M–C(π))	0.24 eV/bond	0.06 eV/bond

Table 6 Raman spectroscopy: wave numbers [cm^{-1}] of C–C stretching vibrations ($\tilde{\nu}(\text{C}\equiv\text{C})$) and C–H stretching vibrations ($\tilde{\nu}(\text{C–H})$) of some ternary ethynylometallates (w: weak, m: medium, ms: medium strong, s: strong, sh: shoulder, br: broad).

	$\tilde{\nu}(\text{C}\equiv\text{C})/\text{cm}^{-1}$	$\tilde{\nu}(\text{C–H})/\text{cm}^{-1}$	Crystal structure
$\text{Na}_2\text{Zn}(\text{C}_2\text{H})_4$	1945	3223	Amorphous
$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$	1943	3264	$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$ type ($\text{I4}_1/\text{a}$, $Z = 4$)
$\text{Rb}_2\text{Zn}(\text{C}_2\text{H})_4$	1939	3260	$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$ type ($\text{I4}_1/\text{a}$, $Z = 4$)
$\text{Cs}_2\text{Zn}(\text{C}_2\text{H})_4$	1936	3206	Unknown
$\text{Na}_2\text{Cd}(\text{C}_2\text{H})_4$	1932	3221	Amorphous
$\text{K}_2\text{Cd}(\text{C}_2\text{H})_4$	1936	3262	$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$ type ($\text{I4}_1/\text{a}$, $Z = 4$)
$\text{Rb}_2\text{Cd}(\text{C}_2\text{H})_4$	1935	3260	$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$ type ($\text{I4}_1/\text{a}$, $Z = 4$)
$\text{Cs}_2\text{Cd}(\text{C}_2\text{H})_4$	1931	3254	$\text{K}_2\text{Zn}(\text{C}_2\text{H})_4$ type ($\text{I4}_1/\text{a}$, $Z = 4$)
$\text{CaCu}(\text{C}_2\text{H})_3 \cdot 6 \text{NH}_3$	1879 (ms)	3239 (sh, br)	$\text{CaCu}(\text{C}_2\text{H})_3 \cdot 6 \text{NH}_3$ type ($\text{P6}_3\text{mc}$, $Z = 2$)
	1893 (s)	3250 (w, br)	
$\text{Rb}_2\text{Cu}(\text{C}_2\text{H})_3 \cdot \text{NH}_3$	1898 (ms)	3261 (w, br)	$\text{Rb}_2\text{Cu}(\text{C}_2\text{H})_3 \cdot \text{NH}_3$ type ($\text{P6}_3/\text{m}$, $Z = 6$)
	1910 (s)		
$\text{Cs}_2\text{Cu}(\text{C}_2\text{H})_3 \cdot \text{NH}_3$	1896 (m)	Not visible	$\text{Rb}_2\text{Cu}(\text{C}_2\text{H})_3 \cdot \text{NH}_3$ type ($\text{P6}_3/\text{m}$, $Z = 6$)
	1908 (s)