Solid State Sciences 4 (2002) 247–253
www.elsevier.com/locate/ssscie

Alkali metal copper acetylides $ACuC_2$ ($A = Na–Cs$): synthesis, crystal structures and spectroscopic properties

Ulrich Cremer [a], Winfried Kockelmann [b,d], Marko Bertmer [c], Uwe Ruschewitz [a,*]

[a] Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany
[b] Mineralogisch-Petrologisches Institut der Universität, Poppelsdorfer Schloß, D-53115 Bonn, Germany
[c] Institut für Makromolekulare Chemie, RWTH Aachen, Worringer Weg 1, D-52074 Aachen, Germany
[d] Rutherford Appleton Laboratory, Chilton, OX11 0QX, Oxford, UK

Accepted 30 October 2001

Abstract

By reaction of CuI and A_2C_2 ($A = K$, Rb, Cs) suspended in liquid ammonia and subsequent heating of the remaining residue in vacuum ternary alkali metal copper acetylides $ACuC_2$ were accessible. $NaCuC_2$ could be obtained by decomposing $NaCu_5C_6$, which was synthesized from NaC_2H and CuI in liquid ammonia. The crystal structures were determined by both X-ray and neutron powder diffraction. In all compounds $^1_\infty[\mathrm{Cu(C_2)}_{2/2}^-]$ chains are the characteristic structural motif. In $NaCuC_2$ and β-$RbCuC_2$ these chains are orientated parallel to the c axis of a tetragonal unit cell ($KAgC_2$ type, $P4/mmm$, $Z = 1$), whereas in $KCuC_2$, α-$RbCuC_2$ and $CsCuC_2$ these chains are arranged in layers perpendicular to the c axis of a tetragonal unit cell ($CsAgC_2$ type, $P4_2/mmc$, $Z = 2$). These layers are staggered along the c axis by rotating them by 90° to each other. The alkali metal ions separate the copper carbon chains. Raman spectroscopic investigations indicate the existence of C–C triple bonds, as the frequencies of the C–C stretching vibration are comparable to those found for acetylene and ternary silver and gold acetylides. In the ^{13}C MAS NMR spectra of $KCuC_2$, $RbCuC_2$ and $CsCuC_2$ the isotropic signals are complicatedly split due to the coupling to the nearby quadrupolar copper nuclei, but the chemical shifts are in the range found for other acetylides with C–C triple bonds. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Acetylides; ^{13}C MAS NMR spectroscopy; Copper; Crystal structure; Neutron powder diffraction; Raman spectroscopy; X-ray powder diffraction

1. Introduction

Recently we were able to synthesize and characterize the first examples of ternary alkali metal transition metal acetylides. Compounds of composition $A_2M^0C_2$ ($A = Na$–Cs; $M^0 = Pd$, Pt) [1–3] could be obtained by solid state reactions of A_2C_2 [4–7] with palladium or platinum at temperatures of about 350°C, whereas compounds of composition AM^IC_2 ($A = Li$–Cs; $M^I = Ag$, Au) [8,9] were accessible by reaction of AC_2H with M^II in liquid ammonia and subsequent heating of the resulting residue. In all these ternary acetylides $^1_\infty[\mathrm{M}^n\mathrm{(C_2)}_{2/2}^{(2-n)-}]$ chains are the common structural motif, which are separated by alkali metal cations. The acetylides of composition AM^IC_2 crystallize in three different structure types depending upon the respective alkali metal. The arrangements of the $^1_\infty[\mathrm{M^I(C_2)}_{2/2}^-]$ chains in these structures can be described by the three simplest rod packings as given in the literature [10].

Unexpectedly, attempts to synthesize the corresponding ternary alkali metal copper acetylides $ACuC_2$ from AC_2H and CuI were only successful for $A = Na$, but a procedure using A_2C_2 suspended in liquid ammonia and CuI led to the compounds $ACuC_2$ with $A = K$, Rb, Cs [11].

In this paper we report on the syntheses and the crystal structures of these new copper acetylides as determined by X-ray and neutron powder diffraction. Additionally, results of Raman and ^{13}C MAS NMR spectroscopic investigations are given.

2. Synthesis

The known synthesis for alkali metal silver and gold acetylides [8,9] could not be extended to the corresponding

---

[*] Correspondence and reprints.
E-mail addresses: ulrich.cremer@uni-koeln.de (U. Cremer), wak@isise.rl.ac.uk (W. Kockelmann), mbertmer@mc.rwth-aachen.de (M. Bertmer), uwe.ruschewitz@uni-koeln.de (U. Ruschewitz).

PII: S1293-2558(01)01234-1

alkali metal copper acetylides $ACuC_2$ ($A = K$, Rb, Cs). The residue obtained after addition of CuI to a solution of AC_2H in liquid ammonia was inhomogeneous as indicated by different colors of the precipitate. On heating also no homogeneous sample could be obtained and a characterization of the product mixture by X-ray powder diffraction failed. Therefore a new synthetic route had to be found and the following synthesis starting from A_2C_2 suspended in liquid ammonia turned out to be successful.

All actions were carried out under argon, since the title compounds are sensitive to air and moisture. In a typical procedure A_2C_2 (0.50 mmol) [6,7] was suspended in liquid ammonia (40 ml) at −78°C. Then CuI (0.50 mmol) [12] was added to the stirred mixture. Immediately an orange solid precipitated. Ammonia was removed by warming the mixture to room temperature and storing in vacuum overnight. After washing with liquid ammonia to remove soluble AI the insoluble product was dried again in vacuum for several hours. Its X-ray powder pattern already showed very broad reflections of $ACuC_2$. After heating in dynamic vacuum ($KCuC_2$: 130°C for 1 h; $RbCuC_2$: 200°C for 3 h; $CsCuC_2$: 200°C for 5 h) the color of the solid changed from orange to gray. An increase of the pressure during this procedure could point to small amounts of adsorbed ammonia in the unheated compounds. Now narrow reflections were found in the corresponding X-ray powder diffractograms of the products. The sample of $KCuC_2$ contained a small amount of an indefinable side-product, whereas two modifications of $RbCuC_2$ were found named α- and β-$RbCuC_2$ (Fig. 1). The overall reaction scheme can be described as follows:

$$A_2C_2 + CuI \rightarrow ACuC_2 + AI, \quad \text{with } A = K, Rb, Cs. \qquad (1)$$

$NaCuC_2$ could be prepared by a synthesis similar to the one successful for ternary silver and gold acetylides [8,9]. After dissolving Na (2.80 mmol) in liquid ammonia (40 ml) at −78°C acetylene was passed over the blue solution, until it decolorized. Then CuI (1.40 mmol) [12] was added to the colorless NaC_2H solution, and immediately the color of the mixture changed to red. It was warmed to room temperature and the remaining residue was dried in vacuum overnight. While heating to 200°C (10 min, dynamic vacuum) the color of the solid changed to orange and the pressure increased. After washing several times with liquid ammonia to remove soluble NaI the product was dried in vacuum overnight. The resulting X-ray powder pattern could be indexed with an orthorhombic unit cell. An ab-initio structural investigation revealed that the orange residue consists of $NaCu_5C_6$ with C_2 dumbbells and short Cu–Cu distances. This new compound is still under investigation and will be subject of a future publication. The complete reaction sequence for $NaCu_5C_6$ is unclear, but the following hypothetical overall scheme seems to be plausible:

$$6\,NaC_2H + 5\,CuI \rightarrow NaCu_5C_6 + 5\,NaI + 3\,C_2H_2. \qquad (2)$$

$NaCuC_2$ was synthesized by heating small amounts of $NaCu_5C_6$ sealed in a glass ampoule under argon (270°C, 1 h). The color of the solid changed from orange to gray. Its X-ray powder diffractogram showed sharp reflections of $NaCuC_2$ besides weak reflections of $NaCu_5C_6$, Cu and another indefinable impurity. A possible reaction scheme is given in (3):

$$NaCu_5C_6 \xrightarrow{270^\circ C,\ 1\ h} NaCuC_2 + 4\,Cu + 4\,C. \qquad (3)$$

It should be mentioned that heating $NaCu_5C_6$ at temperatures below 270°C resulted in mixtures of $NaCuC_2$ and $NaCu_5C_6$ with smaller amounts of $NaCuC_2$.

Attempts to synthesize $LiCuC_2$ were unsuccessful up to now. Only solids amorphous to X-rays could be obtained.

3. Crystal structure determination

The title compounds were analyzed by X-ray powder diffraction (Stoe Stadi P2, Ge monochromator, Cu $K\alpha_1$ radiation, capillaries: $\varnothing = 0.3$ mm, linear position sensitive OED detector; $NaCuC_2$: Huber Image Foil Guinier Camera 670, Ge monochromator, Cu $K\alpha_1$ radiation, capillary $\varnothing = 0.3$ mm) [13] and in case of $KCuC_2$ and $RbCuC_2$ additionally by neutron powder diffraction (ROTAX *time-of-flight* diffractometer at ISIS spallation source (Rutherford Appleton Laboratory, UK [14]), samples in vanadium cylinders: $\varnothing = 8$ mm, height approx. 50 mm, wall thickness approx. 0.1 mm, closed with aluminum screw caps and indium seals air-tight). As the crystal structures of the title compounds are isotypic to the corresponding ternary silver and gold acetylides [8,9] these structures could be used as a starting model for the Rietveld refinements, which were carried out with the GSAS software [15]. The results of the X-ray powder investigations are summarized in Table 1. As carbon atoms are weak scatterers for X-rays compared to copper atoms, no reliable C–C distances could be obtained from the X-ray experiments and were therefore constrained to 120 pm, the expected value for a C–C triple bond [16]. Unfortunately, no improvement with respect to the determination of the C–C distances could be obtained from the neutron diffraction experiments on $KCuC_2$ and $RbCuC_2$. This may have its cause in a bad crystallinity of the samples, which leads to broad reflections and strong reflection overlap, and to anisotropic reflection broadening, which was also found for the analogous silver and gold acetylides and is probably caused by the one-dimensional character of the chain structures. As an example for the quality of the data and the refinements the refined neutron powder pattern of $RbCuC_2$ (10 K, bank 1: $2\theta = 28.75°$) is depicted in Fig. 1, from which it can be deduced that $RbCuC_2$ exists in two modifications indicated by two rows of vertical bars for the positions of the Bragg reflections. Furthermore two weak reflections of an unknown impurity can be seen at $d \approx 300$ and 210 pm, which might also be a reason for the problems in the structural refinements. Therefore the C–C distances had

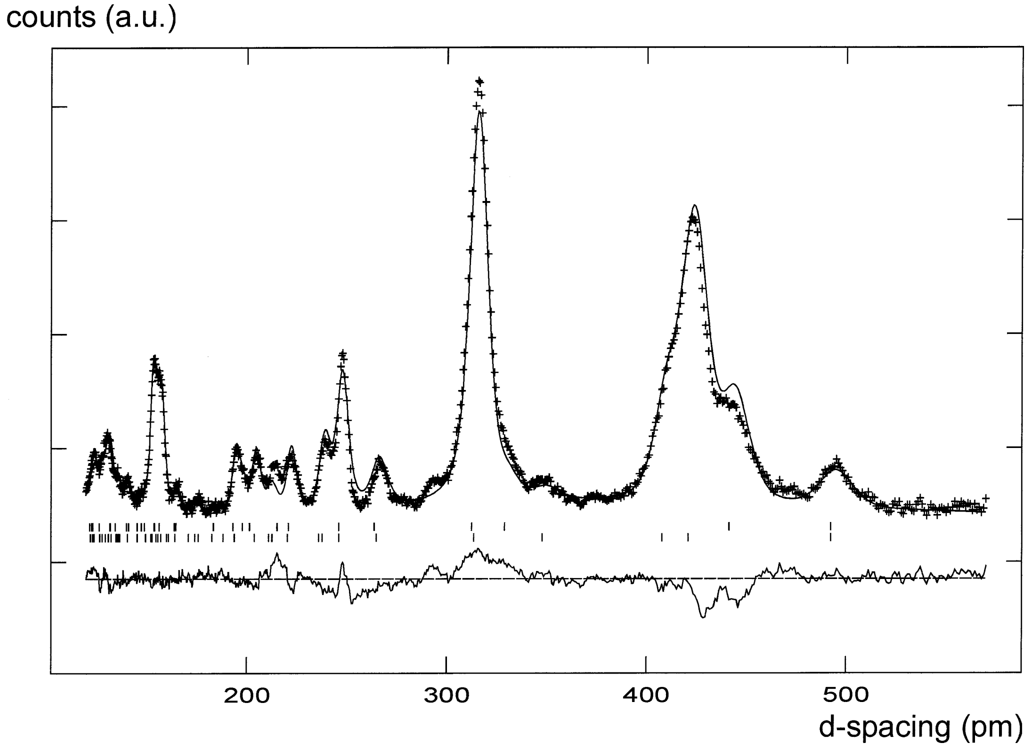

Fig. 1. Neutron diffraction *time-of-flight* pattern ($2\theta = 28.75°$) of $RbCuC_2$ at 10 K, showing the observed (+) and calculated patterns (solid line) as well as the difference between them. Vertical bars mark the positions of the reflections of α-$RbCuC_2$ (lower bars) and β-$RbCuC_2$ (upper bars).

Table 1
Selected crystallographic data of ternary copper acetylides

	$NaCuC_2$	$KCuC_2$	α-$RbCuC_2$	β-$RbCuC_2$	$CsCuC_2$
a (pm)	376.61(2)	490.79(3)	491.79(8)	446.5(1)	494.06(4)
c (pm)	495.95(2)	762.23(6)	832.6(1)	492.5(2)	914.2(1)
V (nm^3)	0.070343(9)	0.18360(3)	0.20137(9)	0.09816(6)	0.22314(6)
Space group	P4/mmm (no. 123)[a]	$P4_2$/mmc (no. 131)[b]	$P4_2$/mmc (no. 131)[b]	P4/mmm (no. 123)[a]	$P4_2$/mmc (no. 131)[b]
Z	1	2	2	1	2
wR_p	0.0269	0.0366	0.0310	0.0310	0.0293
R_p	0.0209	0.0260	0.0241	0.0241	0.0226
R_F	0.0247	0.0476	0.0226	0.0245	0.0440

[a] Cu on 1a, A on 1d, C on 2g with $z \approx 0.378$ (C–C = 120 pm), [b] Cu on 2b, A on 2e, C on 4k with $x \approx 0.122$ (C–C = 120 pm).

to be constrained to 120 pm, the value for a C–C triple bond, using soft constraints. The correctness of this assumption is confirmed by the results of Raman spectroscopic investigations (see Section 4). During these refinements it became obvious that very flat minima exist, as the R-factors for the unconstrained refinements are only slightly lower than those for the constrained ones. The results of the neutron powder investigations on $KCuC_2$ and $RbCuC_2$ are summarized in Tables 2 and 3.

Ternary copper acetylides of composition $ACuC_2$ crystallize in two structure types. $KCuC_2$, α-$RbCuC_2$, and $CsCuC_2$ are isotypic to $CsAgC_2$ ($P4_2$/mmc, $Z = 2$) [8] with $^1_\infty[Cu(C_2)^-_{2/2}]$ chains packed parallel in (0 0 1) layers of the tetragonal unit cell, which are rotated by 90° to each other (Fig. 2). This arrangement corresponds to rod packing (iii) as given by O'Keeffe and Andersson [10]. The alkali metal is coordinated *side-on* by four C_2^{2-} dumbbells in the shape of a tetrahedron. The dumbbells themselves occupy the center of a distorted A_4Cu_2 octahedron. $NaCuC_2$ and β-$RbCuC_2$ are isotypic to $KAgC_2$ (P4/mmm, $Z = 1$) [8] with the anionic copper-carbon chains running all parallel to each other along the c axis of the tetragonal unit cell (Fig. 3) corresponding to rod packing (ii) as given by O'Keeffe and Andersson [10]. Again the C_2^{2-} dumbbell occupies the center of a distorted A_4Cu_2 octahedron and the alkali metal is coordinated *side-on* by four C_2^{2-} dumbbells, but now in the shape of a square.

The K(Rb)–C distances of $KCuC_2$ and α-/β-$RbCuC_2$ (Tables 2 and 3) are in agreement with the values found in binary alkali metal acetylides: K_2C_2 (298 K): 300.9–314.6 pm, (6×) [6]; Rb_2C_2 (Pnma, 298 K): 310.7–387.1 pm, (7×) [7].

Table 2
$KCuC_2$ (see section Supplementary material): summary of neutron powder diffraction investigations (*time-of-flight* method, 3 detector banks, ROTAX at ISIS, Rutherford Appleton Laboratory, Chilton, UK)

	298 K	4 K
Space group	$P4_2/mmc$ (no. 131)	$P4_2/mmc$ (no. 131)
Z	2	2
a (pm)	490.98(3)	492.78(4)
c (pm)	760.78(7)	752.85(8)
V (nm^3)	0.18339(2)	0.18282(3)
K on 2e		
U_{iso} (pm^2)	290(20)	60(10)
Cu on 2b		
U_{iso} (pm^2)	280(10)	26(8)
C on 4k	$x = 0.1223$[a]	$x = 0.1219$[b]
U_{iso} (pm^2)	320(10)	127(8)
No. of reflections	62, 98, 201	61, 217, 625
R_F	0.0750, 0.1367, 0.1511	0.0472, 0.0468, 0.0497
R_p	0.0334, 0.0515, 0.0307	0.0224, 0.0364, 0.0332
wR_p	0.0452, 0.0507, 0.0316	0.0324, 0.0369, 0.0253
No. of refined parameters	36	39
K–Cu (pm)	395.86(2) 8 ×	396.03(3) 8 ×
K–C (pm)	316.30(2) 8 ×	315.82(2) 8 ×
Cu–C (pm)	185.43(4) 2 ×	186.32(4) 2 ×
C–C (pm)	120[a]	120[b]

[a,b] Constrained.

An interesting result of the neutron diffraction experiments is the temperature dependence of the lattice parameters. For $KCuC_2$ and α-$RbCuC_2$ the a axis gets larger with decreasing temperature, whereas the c axis gets smaller. For β-$RbCuC_2$ the a axis decreases with decreasing temperature, whereas the c axis increases. This effect is in agreement with our investigations on other binary and ternary acetylides. It can be explained by a weaker librational motion of the C_2^{2-} dumbbells at low temperatures. As a consequence the unit cell axis parallel to the dumbbell axis increases with decreasing temperature, whereas the other axes decrease as expected.

Comparing the crystal structures of ternary acetylides AM^IC_2 it is obvious that for the larger metals silver and gold the $KAgC_2$ structure type dominates, whereas for the copper compounds the $CsAgC_2$ structure type seems to become more stable. But since for $RbCuC_2$ and $CsAgC_2$ [8] both structure types co-exist, their stability seems to be very similar. In both cases the modification in the $KAgC_2$ structure type has the higher density. Unfortunately, we were not able to find the conditions for synthesizing single-phase products. Also on cooling the molar ratio of both modifications does not change significantly pointing to the fact that no transformation between the two modifications occurs in the temperature range investigated. A third structure type ($LiAgC_2$ structure type, $P\bar{6}m2$, $Z = 1$, corresponding to rod packing (i) as given by O'Keeffe and Andersson [10]) is only found for $LiAgC_2$ and $LiAuC_2$ with the small lithium cation, but we have not been able to synthesize an analogous copper acetylide up to now.

Table 3
$RbCuC_2$ (see section Supplementary material): summary of neutron powder diffraction investigations (*time-of-flight* method, 3 detector banks, ROTAX at ISIS, Rutherford Appleton Laboratory, Chilton, UK)

	298 K	10 K
α-$RbCuC_2$	69.0(3) wt.%	70.3(2) wt.%
Space group	$P4_2/mmc$ (no. 131)	$P4_2/mmc$ (no. 131)
Z	2	2
a (pm)	492.63(6)	493.62(5)
c (pm)	828.5(1)	817.3(1)
V (nm^3)	0.20106(5)	0.19915(4)
Rb on 2e		
U_{iso} (pm^2)	390(20)[a]	95(8)[f]
Cu on 2b		
U_{iso} (pm^2)	90(8)[b]	0(4)[g]
C on 4k	$x = 0.1219$[c]	$x = 0.1219$[h]
U_{iso} (pm^2)	222(9)[d]	101(5)[i]
Rb–Cu (pm)	405.27(4) 8 ×	404.45(3) 8 ×
Rb–C (pm)	327.38(3) 8 ×	326.01(3) 8 ×
Cu–C (pm)	186.24(5) 2 ×	186.66(6) 2 ×
C–C (pm)	120[c]	120[h]
No. of reflections	41, 59, 114	49, 121, 208
R_F	0.0244, 0.0299, 0.0236	0.0284, 0.0183, 0.0156
β-$RbCuC_2$	31.0(3) wt.%	29.7(2) wt.%
Space group	$P4/mmm$ (no. 123)	$P4/mmm$ (no. 123)
Z	1	1
a (pm)	446.12(8)	443.09(7)
c (pm)	491.8(2)	493.4(2)
V (nm^3)	0.09789(6)	0.09687(4)
Rb on 1d		
U_{iso} (pm^2)	390(20)[a]	95(8)[f]
Cu on 1a		
U_{iso} (pm^2)	90(8)[b]	0(4)[g]
C on 2g	$z = 0.3780$[e]	$z = 0.3783$[j]
U_{iso} (pm^2)	222(9)[d]	101(5)[i]
Rb–Cu (pm)	399.98(8) 8 ×	398.78(7) 8 ×
Rb–C (pm)	321.11(5) 8 ×	319.01(5) 8 ×
Cu–C (pm)	185.9(1) 2 ×	186.67(8) 2 ×
C–C (pm)	120[e]	120[j]
No. of reflections	25, 36, 67	32, 72, 123
R_F	0.0296, 0.0327, 0.0264	0.0261, 0.0212, 0.0141
R_p	0.0197, 0.0272, 0.0156	0.0216, 0.0209, 0.0171
wR_p	0.0246, 0.0244, 0.0160	0.0283, 0.0238, 0.0168
No. of refined parameters	41	41

[a–j] Constrained.

4. Raman spectroscopic investigations

The frequencies of the C–C stretching vibration of ternary copper acetylides $ACuC_2$ were determined by means of Raman spectroscopy (Bruker IFS 66v/S with FRAU 106/S, Nd-YAG laser, $\lambda = 1064$ nm, 75–80 mW, 256 scans, samples sealed in glass capillaries under argon). The resulting frequencies are given in Table 4. Surprisingly, no signal could be detected for $NaCuC_2$ even for increased numbers of scans or different laser powers. The resulting frequencies of the C–C stretching vibration in $KCuC_2$, $RbCuC_2$ and $CsCuC_2$ are close to the values obtained for ternary silver and gold acetylides, which are also given in Table 4 [8,9]. Therefore similar C–C bond distances can be assumed in ternary copper and silver acetylides. For the latter neutron diffraction investigations on single-phase products resulted in C–C distances of 122.3(6) pm for $KAgC_2$ and 121.7(7) pm for $CsAgC_2$ [8]. These values are close to the expected value for a C–C triple bond of 120 pm [16]. Thus, the applied value of 120 pm as a C–C soft

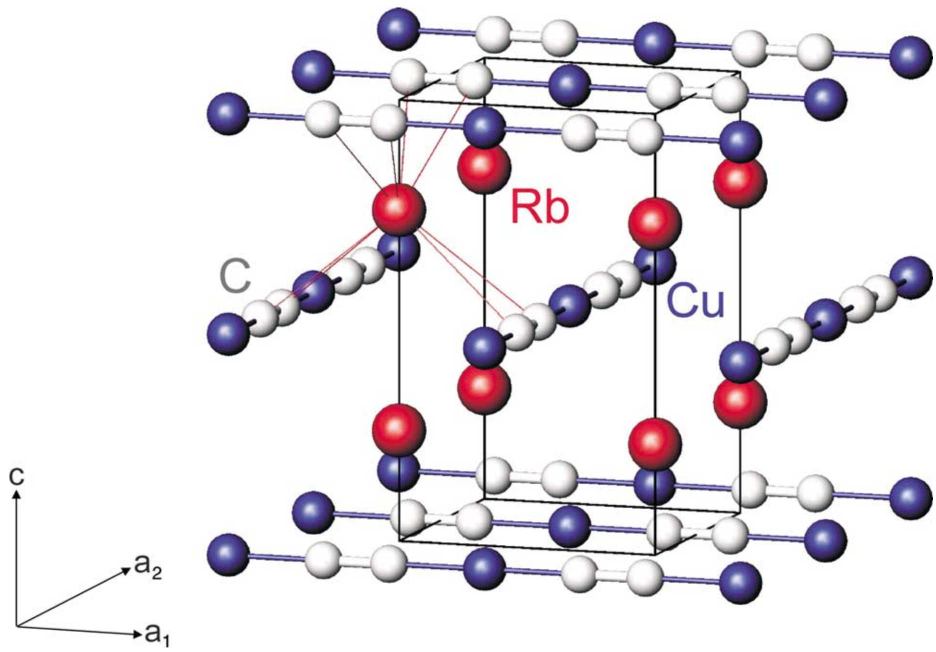

Fig. 2. Crystal structure of α-$RbCuC_2$ ($P4_2/mmc$, $Z = 2$). The unit cell, the C–C and Cu–C bonds as well as the surrounding of one Rb atom are emphasized.

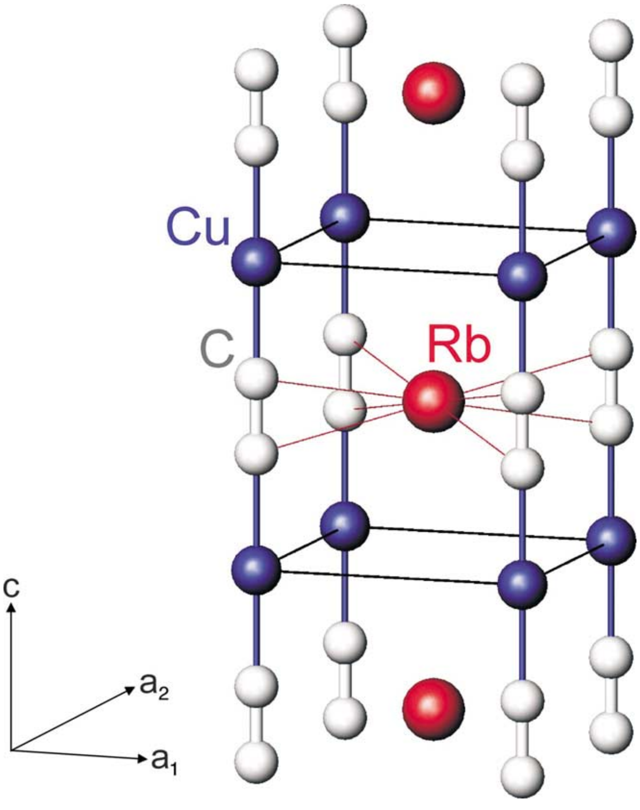

Fig. 3. Crystal structure of β-$RbCuC_2$ ($P4/mmm$, $Z = 1$). The unit cell, the C–C and Cu–C bonds as well as the surrounding of one Rb atom are emphasized.

constraint distance in the Rietveld refinements on $KCuC_2$ and $RbCuC_2$ (see Section 3) is confirmed to be reasonable.

The trend of slightly increasing frequencies of the C–C stretching vibration from the copper to the silver and the gold acetylides (Table 4) was also found in isoelectronic dicyano complexes $[M^I(CN)_2]^-$ regarding the C–N stretching vibration [17,18]. Furthermore it can be seen in Table 4 that the frequencies of the C–C stretching vibration are almost independent of the respective alkali metal. From several experiments on different samples the reproducibility of the frequencies found with the Bruker spectrometer was estimated to 4 cm^{-1}.

The sample of $RbCuC_2$ consists of two modifications, but surprisingly only one signal for the C–C stretching vibration was observed in the Raman spectrum. A close inspection of the spectrum revealed that the full-width-at-half-maximum of this signal is twice as large as the respective signals in $KCuC_2$ and $CsCuC_2$. Thus it must be assumed that the resolution of the Raman spectrometer is not high enough to resolve the signals of the two modifications of $RbCuC_2$ in the present sample.

5. ^{13}C MAS NMR spectroscopy

The acetylides $KCuC_2$, $RbCuC_2$ and $CsCuC_2$ were also examined by means of ^{13}C MAS NMR spectroscopy (Bruker Avance DSX 500, ^{13}C frequency 125.841 MHz, pulse sequence: 90° pulse followed by two 180° pulses with delays of 0.5 µs to remove carbon background signal of the probe [19,20], recycle delay 30 s, spinning rate 5 kHz, number of scans: $KCuC_2$: 7968, $RbCuC_2$: 7776, $CsCuC_2$: 3264, spinning sideband intensities are added up to the isotropic signal). In all spectra (Fig. 4) the carbon resonance line is complicatedly split due to the 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 quadrupole interaction of

Table 4
Raman spectroscopy: frequencies of the C–C stretching vibration in ternary copper, silver and gold acetylides

	$ACuC_2$ $\tilde{\nu}(C{\equiv}C)_{Raman}$ (cm^{-1})	$AAgC_2$ [8] $\tilde{\nu}(C{\equiv}C)_{Raman}$ (cm^{-1})	$AAuC_2$ [9] $\tilde{\nu}(C{\equiv}C)_{Raman}$ (cm^{-1})
A = Li	–[a]	1962	1998
A = Na	–[b]	1965	1997
A = K	1959	1963	1997
A = Rb	1949	1961	1991
A = Cs	1945	1965	1993

[a] Compound unknown, [b] no signal.

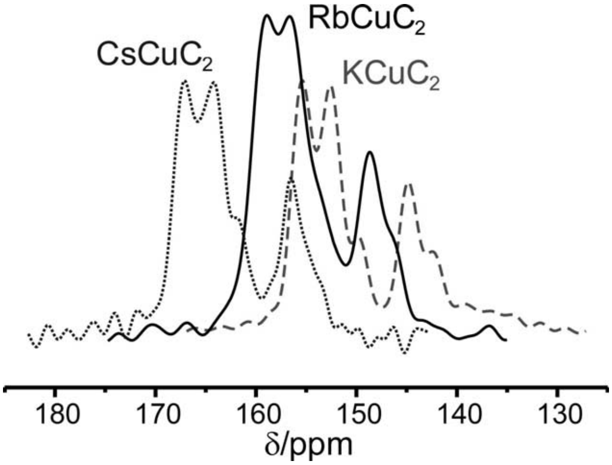

Fig. 4. ^{13}C MAS NMR spectra of $KCuC_2$, $RbCuC_2$ and $CsCuC_2$ (Bruker Avance DSX500; ^{13}C frequency: 125.841 MHz; spinning rate 5 kHz; recycle delay 30 s; number of scans: $KCuC_2$: 7968, $RbCuC_2$: 7776, $CsCuC_2$: 3264); spinning sideband intensities are added up to the isotropic signal.

both copper nuclei has to be considered. This coupling via chemical bonds or through space or both is typical for compounds containing quadrupolar nuclei like copper [21] or chlorine, and therefore a line-shape simulation is currently under investigation [22,23].

From a simple inspection of the spectra it can already be concluded that the chemical shifts increase with an increasing number of electrons of the alkali metal cations. This tendency was also found in binary alkali metal acetylides [6] and ternary alkali metal palladium and platinum acetylides [2]. Furthermore the values of the chemical shifts are in a similar range for all acetylides indicating comparable bonding situations of the carbon atoms in all compounds. Therefore a C–C triple bond seems to be plausible, as a double bond should result in a higher value of the chemical shift. Although a line-shape simulation of the spectra has not been performed yet, it can clearly be seen that a similar coordination of the carbon atoms exists in all three compounds, as the lineshape pattern is nearly identical in their spectra. It is noteworthy at this point that the NMR spectrum of $RbCuC_2$ does not show any distinctive differences to the spectra of $KCuC_2$ and $CsCuC_2$ although the sample of $RbCuC_2$ consists of two modifications. This confirms the similar coordination spheres of the carbon atoms in both modifications (see Figs. 2 and 3).

6. Conclusion

The class of compounds of ternary alkali metal group 11 metal acetylides has been completed by the synthesis of ternary acetylides $ACuC_2$ with A = Na–Cs. Like for silver [8] and gold [9] acetylides of the same composition $^1_\infty[M^I(C_2)^-_{2/2}]$ chains (M^I = Cu, Ag, Au) are the characteristic structural motif, in which the group 11 metal is linearly coordinated *end-on* by two C_2^{2-} dumbbells, the most common coordination of metals with a d^{10} electron configuration. Taking the group 11 metal carbon chains as rods the resulting crystal structures can be understood as the most simple packing arrangements of rods [10], which are separated by the alkali metal ions. These ternary group 11 acetylides exhibit a typical salt-like behavior, as can already be concluded from their colors (M^I = Cu: gray; M^I = Ag: colorless; M^I = Au: yellow). Ternary group 10 acetylides of composition $A_2M^0C_2$ (A = Na–Cs; M^0 = Pd, Pt) however are black and semiconductors with small bandgaps, although their crystal structures are characterized by similar $^1_\infty[M^0(C_2)^{2-}_{2/2}]$ chains. From band structure calculations it could be concluded that A–Pd(Pt) interactions are responsible for these small bandgaps and not, as could be suspected, Pd(Pt)–C interactions [2]. Furthermore, it was found that different C–C distances, as observed in $CsAgC_2$ [8] and Na_2PdC_2 [2], only have a minor influence on the band width of the conduction band, which is responsible for the resulting bandgap. The Na–Pd distances in Na_2PdC_2 are 296.8 pm (3×) [2], the Na–Ag distances in $NaAgC_2$ however are 375.4 pm (8×) [8].

We are now trying to extend the syntheses described above to obtain ternary acetylides of other transition metals like zinc or manganese.

Supplementary material

The supplementary material has been sent to Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. CSD-412037 ($KCuC_2$, 298 K), No. CSD-412038 ($KCuC_2$, 4 K), No. CSD-412039 ($RbCuC_2$, 298 K) and No. CSD-412040 ($RbCuC_2$, 10 K) and can be obtained by contacting the FIZ (quoting the article details and the corresponding CSD number).

Acknowledgements

We thank Dr. Jürgen Huster (X-ray powder diffraction), Dr. Claudia Wickleder (Raman spectroscopy), and Dr. Bodo Zibrowius (NMR spectroscopy) for their help. This work has been financially supported by the Deutsche Forschungsgemeinschaft (DFG).

References

[1] M. Weiß, U. Ruschewitz, Z. Anorg. Allg. Chem. 623 (1997) 1208.

[2] S. Hemmersbach, B. Zibrowius, W. Kockelmann, U. Ruschewitz, Chem. Eur. J. 7 (2001) 1952.

[3] U. Ruschewitz, Z. Anorg. Allg. Chem. 627 (2001) 1231.

[4] M.H. Moissan, C. R. Acad. Sci. 126 (1898) 302;
M.H. Moissan, C. R. Acad. Sci. 127 (1898) 911.

[5] H. Föppl, Angew. Chem. 70 (1958) 401.

[6] S. Hemmersbach, B. Zibrowius, U. Ruschewitz, Z. Anorg. Allg. Chem. 625 (1999) 1440.

[7] U. Ruschewitz, P. Müller, W. Kockelmann, Z. Anorg. Allg. Chem. 627 (2001) 513.

[8] W. Kockelmann, U. Ruschewitz, Angew. Chem. 111 (1999) 3697;
W. Kockelmann, U. Ruschewitz, Angew. Chem., Int. Ed. Engl. 38 (1999) 3492.

[9] J. Offermanns, U. Ruschewitz, C. Kneip, Z. Anorg. Allg. Chem. 626 (2000) 649.

[10] M. O'Keeffe, S. Andersson, Acta Crystallogr., Sect. A 33 (1977) 914.

[11] U. Cremer, U. Ruschewitz, Z. Kristallogr. Suppl. 17 (2000) 128.

[12] G. Brauer, Handbuch der Präparativen Anorganischen Chemie, Vol. II, 3rd edn., F. Enke Verlag, Stuttgart, 1978, p. 975.

[13] STOE WinXPOW, version 1.04, STOE&Cie GmbH, Darmstadt, 1999.

[14] W. Kockelmann, H. Tietze-Jaensch, E. Jansen, W. Schäfer, ROTAX Activity Report 95/96, Rutherford Appleton Laboratory, Chilton, UK, 1997.

[15] A.C. Larson, R.B. v. Dreele, Los Alamos Laboratory, Rep. No. LA-UR 86 (1987) 748, PC version 1.5, 1999.

[16] L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, NY, 1960, p. 230.

[17] G.W. Chantry, R.A. Plane, J. Chem. Phys. 33 (1960) 736.

[18] L.H. Jones, J. Chem. Phys. 27 (1957) 468.

[19] M.R. Bendall, R.E. Gosdon, J. Magn. Reson. 53 (1983) 365.

[20] D.G. Cory, W.M. Ritchey, J. Magn. Reson. 80 (1988) 128.

[21] S. Kroeker, R.E. Wasylishen, J.V. Hanna, J. Am. Chem. Soc. 121 (1999) 1582;
S. Kroeker, R.E. Wasylishen, Can. J. Chem. 77 (1999) 1962.

[22] S.H. Alarcón, A.C. Olivieri, R.K. Harris, Solid State Nucl. Magn. Reson. 2 (1993) 325.

[23] D.W. Alderman, M.S. Solum, D.M. Grant, J. Chem. Phys. 84 (1986) 3717.