A solution of [NEt$_4$]**2** (40 mg, 0.030 mmol) in THF was treated at 273 K with one equivalent of [Re$_2$(CO)$_8$(thf)$_2$]. The temperature was increased to room temperature, then the solution was concentrated to dryness and the residue dissolved in CH$_2$Cl$_2$. IR and NMR spectra showed the formation of a complex mixture containing, besides anion **3**, several unidentified species. Crystals of [NEt$_4$]**3** were obtained by slow diffusion of *n*-hexane into a solution in CH$_2$Cl$_2$. Spectroscopic data of the anion **3** (from isolated crystals): IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2119$vw, 2100mw, 2089w, 2053w, 2031s, 2002ms, 1952ms, 1889mw cm^{-1} (C≡O); ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 193 K): $\delta = -15.42$. The reaction has been repeated several times directly in CD$_2$Cl$_2$ in an NMR tube at 193 K. In all cases the resonance of **3** was the most intense, but many other unattributed resonances were also present.

Received: July 20, 1999 [Z13753IE]
German version: *Angew. Chem.* **1999**, *111*, 3695–3697

Keywords: carbonyl complexes · cluster compounds · hydrides · isolobal relationship · rhenium

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Interpenetrated and Noninterpenetrated Three-Dimensional Networks in the Polymeric Species Ag(tta) and 2Ag(tta) · AgNO$_3$ (tta = tetrazolate): The First Examples of the μ_4-η^1:η^1:η^1:η^1 Bonding Mode for Tetrazolate

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Davide M. Proserpio

The current interest in the self-assembly of polymeric coordination networks[1] has afforded many noteworthy two- and three-dimensional frameworks, which are of potential interest as novel materials.[2] Particular attention is now devoted to the use of new polyfunctional suitably tailored complex ligands that enable a certain control of the structural motifs and/or introduce peculiar features in the solid-state products. However, many interesting polymeric frameworks were also obtained in the past by using simple polydentate aromatic nitrogen heterocycles with five-membered (azoles) or six-membered (azines) rings.[3, 4] While the members of these families with two nitrogen atoms have been extensively used in the area of coordination polymers, and some examples of polymeric nets of triazoles[5] and triazines[6] are known, the networking ability and the full potential donor properties of species containing a higher number of nitrogen atoms, like tetrazoles and tetrazines, are almost completely unknown. Tetrazole (Htta) exists in two tautomeric forms (1*H* and 2*H*, see Scheme 1); it is an acidic species with a pK_a value of about 5, and the anion tetrazolate (tta) is a potentially tetradentate ligand, though in most of the reported adducts it functions as only a mono- or bidentate ligand.[3] Substituted tetrazole derivatives have also been studied for their potential properties as explosives or detonators.

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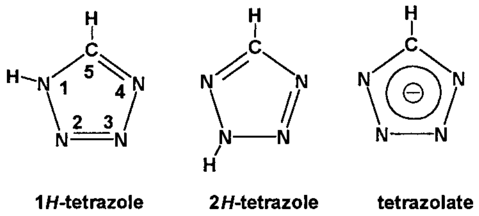

Scheme 1.

The silver salt of tetrazole has been known since 1892[7] and many silver salts of substituted tetrazolates were prepared in the 1950s mainly for analytical purposes,[8] but, nevertheless, the structural properties of these species, suspected to be polymeric, have until now remained unexplored.

We have reinvestigated the reactions of tetrazole (Htta) with different silver salts, and have obtained single crystals of the simple salt [Ag(tta)] suitable for an X-ray structure analysis. The structure comprises a polymeric twofold interpenetrated three-dimensional network, which is formulated as **1**. In addition, in reactions of tetrazole with $AgNO_3$ we have obtained the novel double salt $2\,Ag(tta)\cdot AgNO_3$, which consists of a three-dimensional framework with large channels and is formulated as **2**. While few cases of the μ_3-η^1:η^1:η^1 coordination mode have been observed in tetrazolate derivatives, namely in two trinuclear organometallic rhodium(I) complexes[9] and in the polymeric two-dimensional complex $[Li(\mu_3\text{-tta})]\cdot DMSO$,[10] these are the first examples of the μ_4-η^1:η^1:η^1:η^1 bonding mode for this heterocycle.

$[Ag_2(\mu_4\text{-tta})(\mu_3\text{-tta})]$ **1**

$[Ag_3(\mu_4\text{-tta})_2](NO_3)$ **2**

The reactions of $AgNO_3$, $AgBF_4$, or $Ag(CF_3SO_3)$ with Htta in water/ethanol at room temperature in the molar ratio 1:1 afford good yields of white polycrystalline precipitates that analyze for [Ag(tta)]. Single crystals were grown within a few days by slow evaporation of an ethanolic equimolar solution of $AgBF_4$ and Htta. The X-ray structure revealed that the crystals correspond to **1**.[11] X-ray powder diffraction patterns of all the polycrystalline samples have shown the presence of pure compound **1** by comparison with the pattern calculated from the single-crystal structure. The reaction of $AgNO_3$ with Htta was also investigated in the presence of an excess of the salt. The polycrystalline samples obtained by using a molar ratio of 1:1.5 display a powder diffraction pattern that is completely different from that of **1**. The elemental analysis is consistent with the double salt $2\,Ag(tta)\cdot AgNO_3$. Single crystals were obtained in a few days by layering a solution of Htta in ethanol over a solution of $AgNO_3$ in water (molar ratio 1:1.5). The structure analysis revealed that they correspond to the polymeric species **2**.[11] Also in this case, the X-ray powder diffraction pattern computed from the single-crystal data of **2** was used to assess the purity of the crude polycrystalline samples of this material.

The structure of compound **1** consists of a three-dimensional neutral network based on triconnected and tetraconnected silver centers in the ratio 1:1, which are joined through tetrazolate anions one half of which act as *exo*-tridentate (N^1,N^2,N^4) and one half as *exo*-tetradentate ligands. The triconnected Ag^I ions display a distorted trigonal-planar coordination (Ag–N 2.197(4)–2.328(4) Å, N-Ag-N 110.2(2)–138.4(2)°), while the tetraconnected ones are distorted tetrahedral (Ag–N 2.261(4)–2.410(4) Å, N-Ag-N 94.9(2)–136.6(2)°). The framework can be rationalized by considering that it comprises one-dimensional ribbons (see Figure 1, top) all running in the $[-1\,0\,1]$ direction, in which the inner tta ligands are tetradentate, while the outer ones are tridentate with two nitrogen atoms (N^1,N^2) bridging metal centers inside the ribbon, and the third one (N^4) pointing toward silver atoms of adjacent ribbons. The planes of the ribbons show two mutually perpendicular dispositions (Figure 1, bottom) and each ribbon is connected to four adjacent perpendicular ones, through N-donor (two ribbons) and Ag-acceptor (two ribbons) interactions (dotted lines in Figure 1, bottom). The resulting three-dimensional network has a novel complex (3,4)-connected topology[12] and contains large channels (ca. 6.0×11.1 Å) of rectangular section. Two such identical frameworks interpenetrate in order to fill the voids within the channels (Figure 2).

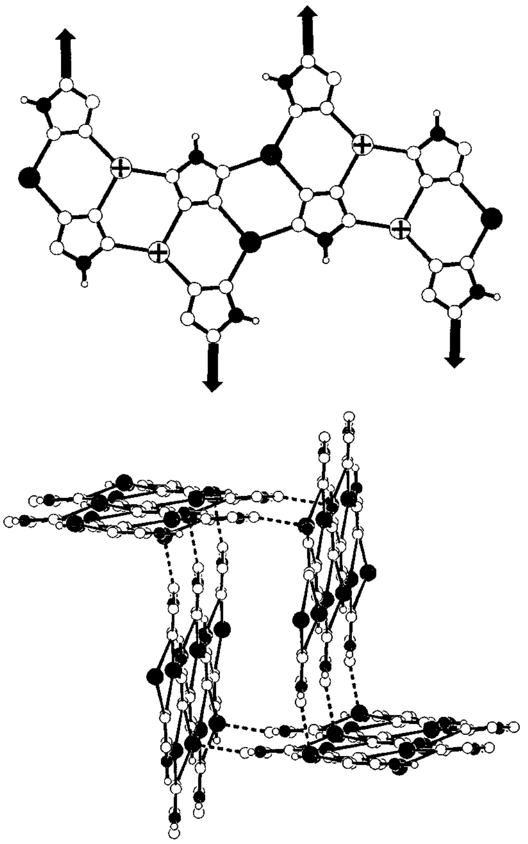

Figure 1. A view of a single ribbon (top) and of the interaction of four such ribbons (bottom) in the polymeric net of compound **1**. Big circles (filled and crossed): silver; medium filled circles: carbon; medium empty circles: nitrogen; small empty circles: hydrogen atoms. In the top view arrows depart from N-donor atoms toward adjacent ribbons, while the acceptor silver atoms (tetraconnected) are crossed. In the bottom view the dotted lines represent the N-donor→Ag-acceptor interactions and hydrogen atoms are omitted for clarity.

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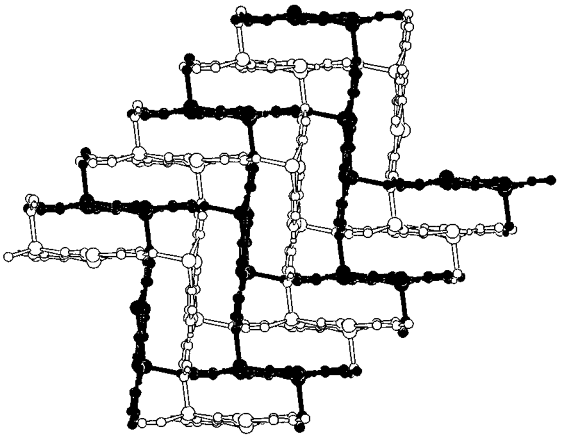

Figure 2. A view of the two interpenetrating nets of compound **1** down [−101] showing the rectangular channels.

Compound **2**[11] consists of a noninterpenetrated three-dimensional cationic framework containing triconnected and biconnected silver centers (ratio 2:1) joined by *exo*-tetradentate tta anions. The triconnected Ag^I ions show a coordination geometry intermediate between T-shaped and trigonal (Ag–N 2.239(3)–2.382(4) Å, N-Ag-N 103.9(1), 109.9(1), 145.8(1)°). These metal centers are joined by (N^1,N^2,N^3)-bridging tta ligands to give undulated two-dimensional layers normal to the [100] direction (Figure 3 top), which comprise four-membered and eight-membered rings and are topologically equivalent to the sheets found in the two-dimensional polymers [Zn(μ_3-1,2,4-triazolate)Cl][5c] and [Li(μ_3-tta)]·DMSO (in which, however, the tta ligand is (N^1,N^2,N^4)-bridging).[10] Each layer of **2** is linked to the adjacent upper and lower layers through the fourth (N^4) nitrogen atoms of tta, which give N-Ag-N bridges with the biconnected silver metals (Ag–N 2.161(3) Å, N-Ag-N 168.1(2)°) acting only as spacers (metal synthons, see Figure 3, bottom). The small deviation from digonal coordination of these metals arises from weak interactions with two oxygen atoms of a nitrate anion (Ag···O 2.685(4) Å). The resulting framework is illustrated in Figure 4, which also shows the anionic channels down [001] containing the nitrate counterions.[12]

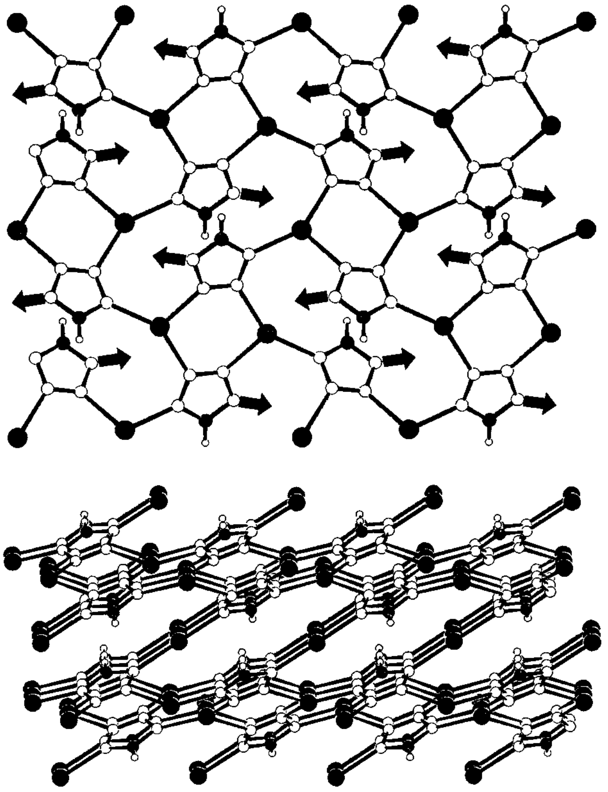

Figure 3. A single undulated layer of $(4\cdot8^2)$ topology, a component of the three-dimensional net in **2**, down the *a* axis (top). Left and right arrows indicate the directions of the N-Ag-N bridges connecting this layer with the adjacent lower and upper ones, respectively. The bottom view presents a pair of such layers linked through the biconnected Ag atoms.

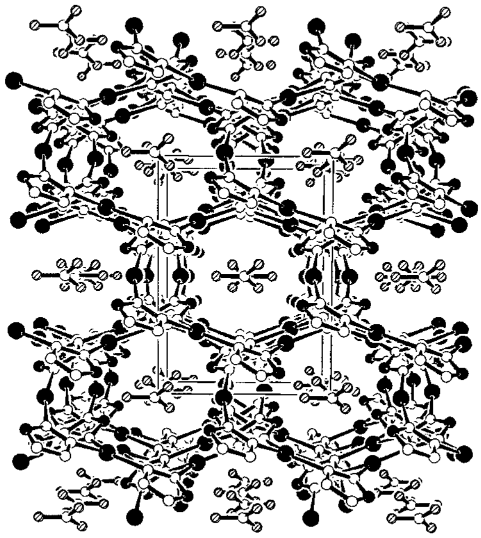

Figure 4. The three-dimensional network of **2**, down the *c* axis, showing the anionic channels containing the nitrates.

In both compounds the silver atoms bound to the tri- and tetradentate tta ligands show significant out-of-plane displacements with respect to the "best plane" of the heterocycle (in the ranges $-0.12/+0.70$ Å (μ^3-tta) and $-0.36/+0.39$ Å (μ^4-tta) for **1** and $-0.64/+0.50$ Å (μ^4-tta) for **2**.

Tetrazolate salts and complexes of the heavy metals are known to be heat- and shock-sensitive, and several (especially 5-subsituted) such complexes have found commercial use as explosives or detonators.[3, 13–15] Tetrazole itself explodes when heated above its melting point (155–156 °C),[13] and many silver tetrazolates decompose with a flash when heated on a spatula.[8] Therefore, thermal analyses of these species must be carried out with caution, on small samples (<0.001 g), and only the use of a slow heating rate[14] can avoid explosion (occurring otherwise for both **1** and **2** at $T \approx 220\,^\circ$C). Differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses of compund **1** have shown that it decomposes with an exothermic peak (at 224 °C) to give a yellow solid phase, recognized as silver(I) cyanamide Ag$_2$CN$_2$ by X-ray powder diffraction and IR spectroscopy, which, on increasing T up to 600 °C, completely converts to silver metal. Compound **2** is somewhat more stable and decomposes in a complex fashion with two exothermic peaks (at 248 and 304 °C) to give a solid mixture of Ag$_2$CN$_2$ and other minor unidentified species, which are completely converted into silver metal at 600 °C.

The results reported show that tetrazolates can employ all the available donor atoms of the aromatic ring and that they are capable of producing robust interesting polymeric networks. This confirms the potentially rich coordination chemistry of these ligands, as revealed by the recent report of another unusual (μ-η^1:η^2) bonding mode of tta in some organolanthanide complexes.[16] Another point of interest is that the existence of the double salt **2** can explain the difficulties encountered by earlier researchers in the analyses of the silver tetrazolates obtained by using an excess of silver nitrate, which were then ascribed to the fact that the precipitates appeared to "occlude or adsorb excess reagent".[8a]

Experimental Section

1: A solution of tetrazole (0.045 g, 0.645 mmol) in EtOH (5 mL) was added to a stirred solution of $AgNO_3$ (0.109 g, 0.639 mmol) in water (5 mL) at room temperature. A white precipitate was immediately formed. The reaction mixture was stirred for 2 h and the resulting precipitate was filtered, washed with ethanol, and dried in the air (yield > 90 %). Elemental analysis (%) calcd for $CHAgN_4$: C 6.79, H 0.570, N 31.68; found C 6.68, H 0.49, N 31.02. Product **1** was also obtained by using $AgBF_4$ and $Ag(CF_3SO_3)$ under the same conditions. The polycrystalline samples obtained from the different silver salts are identical and correspond to pure **1**, as confirmed by X-ray powder diffraction data compared to the spectrum of **1** calculated from single-crystal X-ray analysis. Single crystals of **1** suitable for structural analysis were obtained by slow evaporation of an ethanolic solution of $AgBF_4$ and tetrazole in a molar ratio of 1:1.

2: A white powder of **2** was obtained from a solution of tetrazole (0.041 g, 0.585 mmol) in EtOH (5 mL) and a solution of $AgNO_3$ (0.150 g, 0.877 mmol) in water (5 mL) under the same conditions used for **1** (yield ca. 70 %). The correct tetrazole/$AgNO_3$ molar ratio of 1:1.5 is fundamental in order to avoid the formation of mixtures. Elemental analysis (%) calcd for $C_2H_2Ag_3N_9O_3$: C 4.57, H 0.385, N 24.08; found C 4.32, H 0.40, N 23.92. The purity of the samples of **2** was tested by X-ray powder diffraction.

Both compounds are air- and light-stable for long periods and insoluble in the common solvents. IR (Nujol mull): for **1**: $\tilde{\nu} = 3162$ m, 3086 m, 1443 m, 1141 s, 1131 m, 1077 m, 1029 m, 1003 m, 930 m, 722 m, 685 m cm^{-1}; for **2**: $\tilde{\nu} =$ 3130 m, 1442 s, 1410 vs, 1354 vs, 1314 s, 1209 m, 1141 s, 1107 m, 1016 m, 911 m, 722 w, 687 m cm^{-1}. The IR pattern for **1** is consistent with that in the literature.[17]

Thermal analyses were performed on Perkin-Elmer DSC7 and TGA7 instruments at a heating rate of 2 K min^{-1}, under a flux of nitrogen. Compound **1** decomposed exothermally at 224 °C, with a weight loss of about 25 %. The remaining yellow polycrystalline sample was characterized as silver cyanamide by its IR spectrum (IR(Nujol mull): $\tilde{\nu} = 2018$ sh, 1969 vs, 1935 sh, 1277 m, 1190 m, 631 w cm^{-1}) by comparison with the spectrum in the literature.[18] Moreover, the X-ray powder diffraction pattern showed broad peaks consistent with the cell parameters reported for this poorly characterized species, for which a structure model is not yet available.[19] Silver cyanamide is known to decompose into gases (N_2 and cyanogen) and silver metal.[20] Slow weight loss was observed in the range 250–600 °C, and the final residue was established to be silver metal by X-ray powder diffraction. Similar behavior was observed for compound **2**. After the first exothermic peak (at 248 °C, coupled with a weight loss of about 20 %) a solid mixture was obtained, whose X-ray powder diffraction pattern showed, together with the peaks attributed to Ag_2CN_2, some additional peaks which remain to be clarified. Successive slow weight loss on heating up to 600 °C again gave pure silver metal.

Received: May 12, 1999 [Z13411IE]
German version: *Angew. Chem.* **1999**, *111*, 3700–3704

Keywords: coordination modes · N ligands · networks · silver · tetrazole

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[11] Crystal data for **1**, $C_2H_2Ag_2N_8$: monoclinic, space group $P2_1/n$ (no. 14), $a = 5.758(1)$, $b = 14.679(3)$, $c = 8.312(3)$ Å, $\beta = 94.27(2)^\circ$, $V = 700.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.355$ Mg m^{-3}, final R value 0.0245 for 1070 independent reflections $[I > 2\sigma(I)]$. For **2**, $C_2H_2Ag_3N_9O_3$: monoclinic, space group $C2/c$ (no. 15), $a = 11.129(1)$, $b = 8.000(1)$, $c = 10.956(1)$ Å, $\beta = 98.07(1)^\circ$, $V = 965.78(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.602$ Mg m^{-3}, final R value 0.0325 for 1115 independent reflections $[I > 2\sigma(I)]$. The data collections were performed at 293 K on an Enraf Nonius CAD4 diffractometer for **1** and on a Brüker SMART CCD area detector for **2**, using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), by the ω scan method, within the limits $3 < \theta < 26^\circ$ (**1**), $3 < \theta < 31^\circ$ (**2**). Empirical absorption corrections (ψ scan for **1** and SADABS for **2**) were applied. The structures were solved by direct methods (SIR97) and refined by full-matrix least-squares on F^2 (SHELX-97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms. All the diagrams were generated by using the SCHAKAL 97 program. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120338 and CCDC-120339. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] The topological classification for the tetranodal (3,4)-connected net in **1** is $(4\cdot10^2)_{Ag}(4\cdot8\cdot10)_{tta}(4^2\cdot8^3\cdot10)_{Ag}(4^2\cdot6\cdot8\cdot10^2)_{tta}$ and for the binodal (3,4)-connected net in **2** is $(4\cdot6\cdot8)_{Ag}(4\cdot6^2\cdot8^3)_{tta}$.

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Novel Ternary Alkali Metal Silver Acetylides M^IAgC_2 (M^I = Li, Na, K, Rb, Cs)[**]

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Recently we showed that Na_2PdC_2 and Na_2PtC_2 can be synthesized by the reaction of Na_2C_2 with palladium or platinum at temperatures of about 350 °C under an inert atmosphere.[1] These compounds are the first examples of ternary alkali metal transition metal acetylides. Their crystal structures are characterized by $^1_\infty[M(C_2)^{2-}_{2/2}]$ chains (M = Pd, Pt) that are separated by sodium ions. In the meantime we were able to extend this synthesis to the analogous potassium, rubidium, and cesium acetylides,[2] but attempts to synthesize ternary acetylides of transition metals other than palladium or platinum by this method were not successful up to now. In 1963 a synthesis was described by which the ternary silver acetylide $KAgC_2$ could be obtained.[3] The crystal structure of this compound was not determined, but elemental analyses and IR investigations corroborated its existence. As highly explosive Ag_2C_2 was used in this synthesis [Eq. (1)], we have tried to find a different approach, which avoids this starting material.

$$2\,KC_2H + Ag_2C_2 \longrightarrow KAgC_2 + K[Ag(C_2H)_2] \qquad (1)$$

For that purpose we treated KC_2H with AgI in liquid ammonia, which resulted in a nonexplosive complex hydrogenacetylide as intermediate [Eq. (2)], which could be transformed into the ternary silver acetylide by heating under high vacuum to temperatures of about 120–130 °C [Eq. (3)].

$$2\,KC_2H + AgI \longrightarrow K[Ag(C_2H)_2] + KI \qquad (2)$$

$$K[Ag(C_2H)_2] \longrightarrow KAgC_2 + C_2H_2 \qquad (3)$$

The by-product KI [Eq. (2)] was removed by washing with liquid ammonia so that the insoluble $KAgC_2$ could be obtained in a pure form. It was possible to extend this synthesis to ternary silver acetylides of the other alkali metals. In a variation, the synthesis of $LiAgC_2$ according to Equation (3) was performed in boiling pyridine. LiI is soluble in pyridine so that the insoluble $LiAgC_2$ could be separated by filtration. All products are colorless, nonexplosive, and sensitive to air and moisture.

X-ray diffractometer investigations[4] on the colorless powders of the silver acetylides resulted in the unit cells and space groups given in Table 1.[5] It is striking that in all unit cells a lattice parameter of about 5.30 Å is found. As this distance corresponds approximately to the sum of two Ag–C single bonds (2.087 and 2.108 Å in $Ag_2C_2 \cdot 2\,AgClO_4 \cdot 2\,H_2O$)[6] and one C–C triple bond (1.206 Å),[7] it was assumed that $^1_\infty[Ag(C_2)^{-}_{2/2}]$ chains run along this unit cell axis. However, the unit cells given in Table 1 suggest that at least three different packing variants of the silver–carbon chains must exist. With these assumptions, possible structural models were created, and the refinements of the X-ray powder diffractograms showed that $NaAgC_2$, $KAgC_2$, and $RbAgC_2$ are isotypic, but $LiAgC_2$ and $CsAgC_2$ crystallize in different structure types. To obtain precise bond lengths neutron powder diffraction experiments on a representative of each structure type (LiAgC2, KAgC2, and CsAgC2) were performed.[8] The resulting crystal structures are shown in Figures 1–3.[9]

Table 1. Lattice parameters of ternary silver acetylides M^IAgC_2 (M^I = Li, Na, K, Rb, Cs) at room temperature.[4]

	a [pm]	*c* [pm]	Space group
$LiAgC_2$	379.6(1)	533.0(1)	$P\bar{6}m2$
$NaAgC_2$	374.7(1)	532.0(1)	$P4/mmm$
$KAgC_2$	424.5(1)	530.7(1)	$P4/mmm$
$RbAgC_2$	447.5(1)	531.0(1)	$P4/mmm$
$CsAgC_2$	527.7(1)	857.9(1)	$P4_2/mmc$

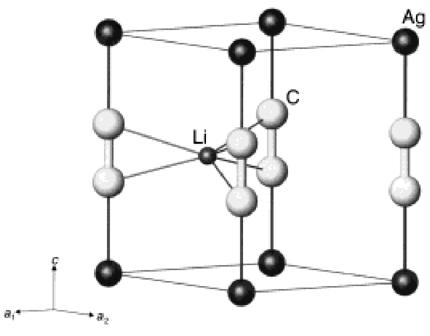

Figure 1. Crystal structure of $LiAgC_2$. The unit cell, the C–C and Ag–C bonds as well as the shortest Li–C distances are emphasized. Selected interatomic distances [Å]: Li–C 2.2786(9) (6 ×), Ag–C 2.025(3) (2 ×), C–C 1.278(6).

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[**] This work was supported by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft. We thank Dr. Krista Kneip for the Raman spectra, Dr. Gregory A. Landrum for the LMTO calculations, and Ulrich Cremer for assistance with the syntheses.