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# The Binary Silver Nitrogen Anion $[Ag(N_3)_2]^-$

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The syntheses of various binary main group azides was achieved during the past decades.[1] However, because of their explosive nature and sensitivity toward shock and friction, such materials are very challenging to handle in most cases. The chemistry and properties of binary transition metal azides are discussed in detail in several reviews.[1a,b,2] Neutral binary azides of the coinage elements (copper, silver, and gold) are the well-known $CuN_3$, $Cu(N_3)_2$, and $AgN_3$ (for their crystal structures please see ref 3). Another binary silver nitrogen compound, the well-known silver nitride $Ag_3N$, is reported to be an extremely sensitive explosive material.[4] Despite several reports in the older literature, which recounted more or less severe explosions during various attempts of isolation and characterization from mixtures of $AuCl_3$ with sodium azide in the preparation of the neutral binary gold azides $AuN_3$ or $Au(N_3)_3$,[5] the existence of both materials remains unconfirmed.[6] Among those references, the possible reducing ability of azide toward Au(III) to result in a hypothetical $AuN_3$ was discussed. Anionic binary azide salts of gold are prepared and unambiguously characterized, such as the azidoaurates $[Au(N_3)_2]^-$ and $[Au(N_3)_4]^-$.[6,7a,8] The azidocuprates $[Cu_2(N_3)_6]^{2-}$ and $[Cu(N_3)_4]^{2-}$ are also fully characterized including their crystal structures.[7] The only report of a possible azidoargentate involves the somewhat questionable high pressure reaction of $CsN_3$ with $AgN_3$, which was characterized only by IR spectroscopy.[9] Other earlier reports dealing with some $[AgX_2]^-$ anions discuss solubility products and instability constants, but comprise incomplete evidence for the formation of a proposed $[Ag(N_3)_2]^-$ species.[10] Another silver−pseudohalogenide anion, the dicyanoargentate $[Ag(CN)_2]^-$, has been synthesized (initially detected by conductometric and potentiometric titration studies in liquid hydrogen cyanide) and characterized including its crystal structure.[11]

During the preparation of the new triphenylsulfonium azide by reaction of triphenylsulfonium bromide with silver azide,[12] a second product was formed and analyzed. Crystals of this byproduct were surprisingly found to consist of a silver-containing anion, the diazidoargentate(I) $[Ag(N_3)_2]^-$ (**1**) [eqs (1a)/(1b)].

$$[Ph_3S]Br + AgN_3 \xrightarrow{CH_3CN} [Ph_3S]N_3 + AgBr \tag{1a}$$

$$[Ph_3S]N_3 + AgN_3 \xrightarrow{CH_3CN} [Ph_3S][Ag(N_3)_2] \quad (\mathbf{1}) \tag{1b}$$

$$[Ph_4P]N_3 + AgN_3 \xrightarrow{CH_3CN} [Ph_4P][Ag(N_3)_2] \quad (\mathbf{2}) \tag{2}$$

The colorless solution of $[Ph_3S]Br$ turned immediately reddish when $AgN_3$ was added to the solution, and AgBr as precipitate was obtained. The same reaction was performed with an excess of $AgN_3$, with the intention to form exclusively this diazidoargentate salt **1**, which is colorless in pure form. A reddish solution was obtained again, but upon removal of all volatile materials a light-red solid was obtained, which was shown to consist mainly of $[Ph_3S]N_3$ and **1**. The color results from another yet unknown material, which was identified as deep-red crystals under the microscope. However, the crystal quality of this material was not sufficient for an X-ray structure analysis.

Consequently, different cations were tested in order to examine the diazidoargentate formation. The reaction of tetraphenylphosphonium azide with 1 equiv of silver azide [eq (2)] furnished the tetraphenylphosphonium diazidoargentate $[Ph_4P][Ag(N_3)_2]$ (**2**) with yields in the range of 30−40%. The reaction mixture had to be stirred for a minimum of 2 days to give a colorless solution of **2** with a significant amount of a gray precipitate, which mostly consists of $AgN_3$ and some other unidentified material. In analogy to the preparation of **1** [eqs (1a)/(1b)], using $[Ph_4P]Cl$ for a reaction with 2 equiv of $AgN_3$ furnished also the diazidoargentate salt **2**. Both salts **1** and **2** are quite light sensitive and burn when exposed to a flame but are not explosive (which is likely an effect of the sterically demanding cations).

Colorless crystals of **1** and **2** were obtained by maintaining acetonitrile solutions (for **1** covered with *n*-hexane) at ambient temperature for several days.[13,14] Both salts crystallize in monoclinic crystal systems (*Cc* and *P*2/*n* with four molecules in the unit cell).

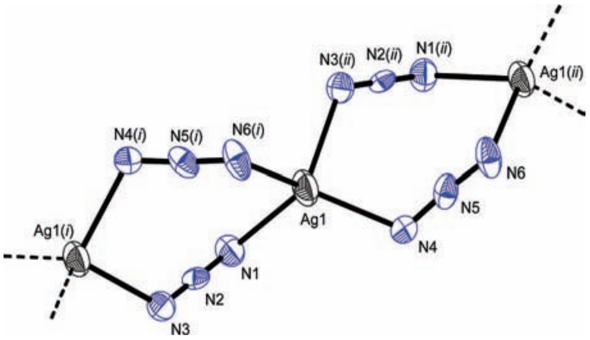

***Figure 1.*** Crystal structure of the anion in **1** with coordination around the silver atom. Selected distances [Å] and angles [deg]: Ag1−N1, 2.331(5); Ag1−N4, 2.291(5); N1−N2, 1.183(7); N2−N3, 1.171(7); N4−N5, 1.194(8); N5−N6, 1.153(8); Ag1−N6(*i*), 2.298(5); Ag1−N3(*ii*), 2.322(5); N1−Ag1−N4, 115.93(18); N1−N2−N3, 178.3(7); N4−N5−N6, 176.2(7); Ag1−N1−N2, 113.8(4); Ag1−N4−N5, 117.7(4); N1−Ag1−N6(*i*), 91.19(18); N4−Ag1−N3(*ii*), 90.36(18); N3(*ii*)−Ag1−N6(*i*), 104.9(2); N3(*ii*)−Ag1−N1, 122.51(18); N4−Ag1−N6(*ii*), 135.1(2); with $i = x, 2 - y, {}^1/_2 + z$, $ii = x, 2 - y, -{}^1/_2 + z$.

In the structure of the sulfonium salt **1** (Figure 1) the azide moieties exhibit almost linear arrangements [N1−N2−N3 178.3(7)° and N4−N5−N6 176.2(7)°] with two only marginally different N−N distances, the $N_\alpha-N_\beta$ distances [N1−N2, 1.183(7) and N4−N5, 1.194(8) Å] being only very slightly elongated compared to the $N_\beta-N_\gamma$ distances [N2−N3, 1.171(7) and N5−N6, 1.153(8) Å]. This finding is in accordance with the structures of $AgN_3 \cdot 2AgNO_3$[15] and $[(PPh_3)_2Ag(\mu\text{-}N_3)_2Ag(PPh_3)_2]$,[16] but in contrast to

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the structure of $AgN_3$ where isolated linear, symmetrical azide moieties exist.[3f] The silver atom is distorted tetrahedrally coordinated by four nitrogen atoms with nearly equal Ag−N bonds. These distances [Ag1−N1, 2.331(5); Ag1−N4, 2.291(5); Ag1−N6(*i*), 2.298(5); and Ag1−N3(*ii*), 2.322(5) Å] are in the range of those found in the structures of $AgN_3$ (2.559 Å),[3f] $AgN_3 \cdot 2AgNO_3$ (2.278−2.503 Å),[15] and $[(PPh_3)_2Ag(\mu\text{-}N_3)_2Ag(PPh_3)_2]$ (2.294 and 2.451 Å).[16] All N−Ag−N angles are in the range between 90° [N4−Ag1−N3(*ii*)] and 135° [N4−Ag1−N6(*i*)]. The motif of bridging $\mu^2$-azide anions, as previously also observed in $[Ag_2(N_3)_2(C_2H_8N_2)]$,[17] furnishes infinite chains along the *c*-axis.

In the structure of the phosphonium salt **2** the anion consists of isolated dimeric $[(N_3)Ag(\mu\text{-}N_3)_2Ag(N_3)]$ units and is shown in Figure 2.

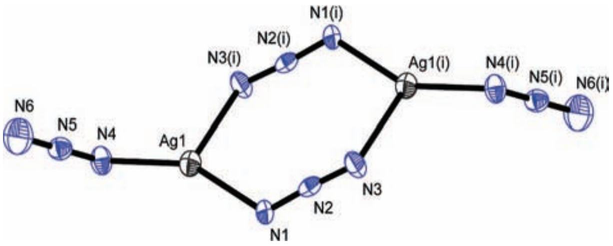

***Figure 2.*** Dimeric unit of the anion in the crystal structure of **2**. Selected distances [Å] and angles [deg]: Ag1−N1, 2.179(4); Ag1−N4, 2.139(4); N1−N2, 1.195(6); N2−N3, 1.173(6); N4−N5, 1.180(6); N5−N6, 1.154(6); Ag1−N3(*i*), 2.485(5); N1−Ag1−N4, 152.07(17); N1−Ag1−N3(*i*), 101.00(15); N4−Ag1−N3(*i*), 103.70(16); N1−N2−N3, 176.1(5); N4−N5−N6, 176.8(6); with $i = 1 - x, 1 - y, -z$.

As previously observed with **1**, both azide moieties exhibit nearly linear arrangements [N1−N2−N3, 176.1(5)°; N4−N5−N6, 176.8(6)°] with again only slightly elongated $N_\alpha - N_\beta$ bonds [N1−N2, 1.195(6); N4−N5, 1.180(6) Å] compared to the $N_\beta - N_\gamma$ bonds [N2−N3, 1.173(6); N5−N6, 1.154(6) Å]. The Ag−N bond distances consist of two slightly shorter [Ag1−N1, 2.179(4); Ag1−N4, 2.139(4) Å] and one elongated bond [Ag1−N3(*i*), 2.485(5) Å] compared to the values in **1**. In contrast to the polymeric anion in the structure of the sulfonium salt **1**, only one additional silver−nitrogen contact is present in **2**, creating a dimeric unit, which in our opinion results from the increased cation size. The formation of polymeric chains of this anion in **1** can be explained by the twist of the azido groups out of a linear N−Ag−N angle. In contrast, the linear arrangement in $[Ag(CN)_2]^-$ does not allow such secondary Ag•••N contacts. The crystal structures of those dicyanoargentate salts are characterized by secondary Ag•••Ag contacts between the anions and do not show cation dependent structures ($Na^{+}$[11b], $Ph_3Te^{+}$[11c]). There is no comparison to $[Cu(N_3)_2]^-$ and $[Au(N_3)_2]^-$ possible, since their crystal structures are unknown. In the crystal structure of the Au(III) azide anion, $[Ph_4As][Au(N_3)_4]$ isolated $[Au(N_3)_4]^-$ moieties and typical N−N distances for covalent azide groups are present.[6a,8b] In the crystal structure with the smaller tetramethylammonium cation, $[Me_4N][Au(N_3)_4]$ displays a polymeric stacking of the anion with Au•••Au contacts.[8c] Several structures of the azidocuprates $[Cu_2(N_3)_6]^{2-}$ and $[Cu(N_3)_4]^{2-}$ with different cations were determined and also show various anion coordinations.[7]

In the $^{14}N$ NMR spectra of **2** two resonances at $\delta = -132$ and $-285$ ppm are visible and portend more the typical pattern of an ionic azide compound, rather than the three expected resonances for covalent azide species. The Raman spectrum also supports the presence of such an ionic species, also because a band for the symmetric $N_3$-vibration is visible at 1328 $cm^{-1}$. Taking into account the bonding situation of the discussed crystal structures of **1** and **2**, the resonances for ionic species in solution seem to be likely. In the structure of **1** (Figure 1) the $N_\alpha$ and $N_\gamma$ nitrogen atoms are not distinguishable, and therefore in the $^{14}N$ NMR spectrum only one resonance for both terminal nitrogens is found. In the case of **2** (Figure 2) two different azide moieties are present and five resonances would be expected, which could not be observed. The $[Ph_4P]$-salt **2** shows a single resonance in the $^{109}Ag$ NMR spectrum ($\delta = 453$ in $CDCl_3$, 479 ppm in $CD_3CN$), which is in the region of the resonance of the comparable dicyanoargentate salt $[Ph_3Te][Ag(CN)_2]$ ($\delta = 593$ ppm in $CDCl_3$),[11c] and few other argentate(I) salts observed in the solid state.[18]

The gas phase structure of the $[Ag(N_3)_2]^-$ anion was initially calculated at the MPW1PW91/SDD level of theory using a large core for silver with 46 electrons (method I).[19] Both isomers, the experimentally observed $C_{2v}$ structure and the $C_{2h}$ structure shown in Figure 3 were found to be stable minima on the potential energy hypersurface with $\Delta E = 0.0$ kcal $mol^{-1}$ (including zero-point correction).

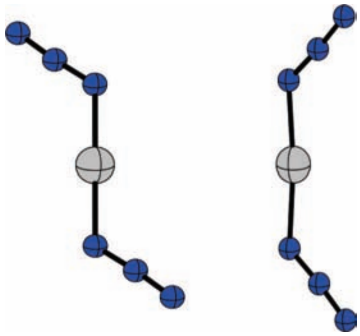

***Figure 3.*** Calculated structure of the anion $[Ag(N_3)_2]^-$ ($C_{2h}$-isomer left, $C_{2v}$-isomer right).

The computed Ag−N distances ($C_{2v}$) are with 2.05 Å significantly shorter than the experimental values of **1** [2.331(5)/2.291(5) Å] and **2** [2.179(4)/2.139(4) Å]. This may be explained by strong interionic interactions in the crystal. At the same DFT level of theory we then applied a small-core MWB pseudopotential for silver (ECP-28-MWB) and a large valence basis set of the following contraction: (8s7p6d2f1g)/[6s5p3d2f1g],[20] for N a cc-pVDZ valence basis set was used (method II). The small core calculation again revealed that both isomers are stable minima essentially identical in their energy with the $C_{2h}$ isomer being favored over the $C_{2v}$ structure by only 0.01 kcal $mol^{-1}$ (including zero-point correction). Again, for both structures the calculated Ag−N distances are 2.05 Å. To account for the significantly shorter calculated values compared to the experimental Ag−N distances, the dimer in $C_i$ symmetry (methods I and II) was also computed and resulted in the dissociation of the dimer at both levels into two separate $C_{2h}$ $[Ag(N_3)_2]^-$ moieties.

The difference between the calculated (gas phase) and observed (X-ray, solid state) structure can best be explained by the fact that the isolated ion in the gas phase has considerable covalent bonding character between the Ag and the $N_3$ units. In the condensed phase, however, due to interionic interactions the bonding is largely ionic with the azide units corresponding to $N_3^-$ ions with virtually identical N−N distances (within $3\sigma$).

Subsequent reactions performed with other cations, tetramethylammonium and bis(triphenylphosphoranylidene)-ammonium (PNP), did not result in the formation of corresponding diazidoargentate salts $Cat[Ag(N_3)_2]$ (Cat = $Me_4N$, PNP). All reactions were carried out under same conditions such as temperature, solvent, and reaction time. It seems that the reaction is strongly dependent on the size of the cation. Whereas the $[Me_4N]^+$-cation seems to be too small, the extremely bulky $[PNP]^+$-cation also hinders the reaction. A possible explanation for the instability of a $[PNP][Ag(N_3)_2]$ salt might be that the very large cation causes the anion to become monomeric and that the monomeric anion is too unstable and abstracts an azide anion.

In summary, we were able to synthesize and determine the crystal structures of two different salts of the novel diazido-argentate anion. Slight changes of the nature of the cation produce different characteristics in the silver−nitrogen contacts in the solid state of the triphenylsulfonium and tetraphenylphosphonium salts.

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**Supporting Information Available:** Complete ref 19; computational results, comparison of calculated and observed vibrational frequencies, cif files of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Experimental procedure: *CAUTION! Silver azide is an extremely hazardous and explosive material. All compounds should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather suits, gloves, and ear plugs). Ignoring these safety precautions can result in serious injury!* NMR spectra were recorded at 25 °C on a JEOL Eclipse 400 instrument, and chemical shifts are with respect to $MeNO_2$ ($^{14}N$, 28.9 MHz), and 2 M $AgNO_3/D_2O$ ($^{109}Ag$, 18.6 MHz). **$[Ph_3S][Ag(N_3)_2]$ (1):** Into a solution of $[Ph_3S]Br$ (0.29 mmol) in $CH_3CN$ (4 mL) was added $AgN_3$ (0.58 mmol) at ambient temperature. The solution immediately turned red-brownish and a precipitate (AgBr) was obtained. After being stirred for 3 days at ambient temperature, the solution was filtrated, and all volatile materials were removed in vacuo yielding a pale reddish solid. Besides the major product $[Ph_3S]N_3$, **1** was found as a by-product (estimated yield 10−30%). IR and Raman data could not be observed in sufficient quality and is therefore not reported. $^{14}N$ NMR ($CDCl_3$) $\delta$:−137 ($N_\beta$, 1N),−280 ($N_\alpha/N_\gamma$, 2N) ppm. **$[Ph_4P][Ag(N_3)_2]$ (2):** Into a solution of $[Ph_4P]N_3$ (0.52 mmol) in $CH_3CN$ (8 mL) was added $AgN_3$ (0.52 mmol) at ambient temperature. After being stirred for 3 days, a colorless precipitate was obtained which was filtered off the solution. All volatile materials were removed in vacuo yielding a colorless solid (estimated yield 30−40%). IR (Nujol mull): $\nu = 3423$ (br), 3079 (w), 2036/2012/1993 (vs) ($\nu_{as}N_3$), 1633 (s), 1473 (s), 1443 (vs), 1401 (m), 1316 (w), 1180 (w), 1158 (w), 1064 (m), 1021 (w), 996 (m), 937 (w), 850 (w), 834 (w), 755 (vs), 684 (vs), 500 (s) $cm^{-1}$. Raman (neat solid, fluorescence): $\nu = 3064$ (80), 1578 (80), 1328 (48), ($\nu_sN_3$), 1181 (29), 1162 (28), 1079 (53), 1027 (56), 1002 (100), 688 (30), 613 (23), 498 (15), 259 (43), 213 (28) $cm^{-1}$. $^{14}N$ NMR ($CDCl_3$) $\delta$:−132 ($N_\beta$, 1N),−285 ($N_\alpha/N_\gamma$, 2N) ppm. $^{109}Ag$ NMR $\delta$: 453 ($CDCl_3$); 479 ($CD_3CN$) ppm. (b) Klapötke, T. M.; Krumm, B.; Scherr, M. $[Ph_3S]N_3$ fully characterized incl. X-ray crystallography, submitted for publication.

(13) Crystal data for **1**, $C_{18}H_{15}AgN_6S$: $M_r = 455.29$, monoclinic, space group *Cc*, $a = 16.3409(12)$, $b = 10.5219(8)$, $c = 10.6388(6)$ Å, $V = 1824.3(2)$ Å$^3$, $F(000) = 912$, $\rho_{calcd}$ ($Z = 4$) $= 1.658$ g $cm^{-3}$, $\mu = 1.234$ $mm^{-1}$, approximate crystal dimensions 0.15 × 0.10 × 0.09 $mm^3$, $\theta$ range = 3.8−26.0°, Mo Kα ($\lambda = 0.71073$ Å), $T = 200$ K, 8433 measured data (Oxford Xcalibur3 diffractometer with a CCD area detector), of which 3522 ($R_{int} = 0.0447$) unique. Structure solution by direct methods, full-matrix least-squares refinement on $F2$, data to parameters ratio: 15.0:1, final $R$ indices [$I > 2\sigma(I)$]: $R1 = 0.0370$, $wR2 = 0.0686$, $R1 = 0.0616$ (all data), $wR2 = 0.0796$ (all data), GOF on $F2 = 1.041$. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition number CSD-692513.

(14) Crystal data for **2**, $C_{24}H_{20}AgN_6P$: $M_r = 531.30$, monoclinic, space group *P2/n*, $a = 16.4246(7)$, $b = 7.3362$, $c = 19.1152(8)$ Å, $V = 2242.24(17)$ Å$^3$, $F(000) = 1072$, $\rho_{calcd}$ ($Z = 4$) $= 1.574$ g $cm^{-3}$, $\mu = 0.995$ $mm^{-1}$, approximate crystal dimensions 0.31 × 0.18 × 0.06 $mm^3$, $\theta$ range = 3.8−26.0°, Mo Kα ($\lambda = 0.71073$ Å), $T = 135$ K, 12464 measured data (Oxford Xcalibur3 diffractometer with a CCD area detector), of which 4383 ($R_{int} = 0.0408$) unique. Structure solution by direct methods, full-matrix least-squares refinement on $F2$, data to parameters ratio: 15.1:1, final $R$ indices [$I > 2\sigma(I)$]: $R1 = 0.0308$, $wR2 = 0.0814$, $R1 = 0.0517$ (all data), $wR2 = 0.0885$ (all data), GOF on $F2 = 0.981$. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition number CSD-692514.

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