provides additional corroboration. The polarization pattern of the top trace in Figure 1 must therefore be due to the radical Met-(S$\overset{+}{\therefore}$N) of methionine with the two-center three-electron bond.

In our high magnetic field (5.9 T) and with the substantial difference Δg of the radical pair involved, there is approximate proportionality between polarization intensity and the hyperfine coupling constant.[8] Furthermore, it is reasonable to assume that the formation of Met-(S$\overset{+}{\therefore}$N) from the sulfur-centered radical cation Met(S$^{\dot{+}}$)—which must be the primary methionine-derived radical because in the ground state the interaction between the lone pairs of sulfur and nitrogen is repulsive—is fast on the CIDNP timescale because this reaction is exergonic and the rate-limiting step should be diffusion of the linked sulfur and nitrogen moieties towards one another. Under these conditions the distribution of the unpaired spin density ϱ in the radical cation Met-(S$\overset{+}{\therefore}$N) can be estimated from the limiting ratio of CIDNP intensities P (H^1): P (H^3) at high pH by using McConnell-type relationships.[12] Taking the dimeric radical cation of tetrahydrothiophene (a (H$^{\alpha}$) = 0.93 mT;[14] this value must be doubled to describe a radical cation in which ϱ is located on a single sulfur atom) and the radical cation of N-methylpyrrolidine (average of the splittings the methylene α protons 4.25 mT)[15] as model compounds, one obtains that in the species Met-(S$\overset{+}{\therefore}$N) with the two-center three-electron bond about one third of the unparied spin density is shifted from sulfur to nitrogen ($\varrho_S:\varrho_N = 0.64:0.36$). The calculated ratio ($\varrho_S:\varrho_N = 0.74:0.26$)[7] is somewhat higher but, as the authors of reference [7] pointed out, the STO-3G* method used underestimates the spin density at nitrogen.

Received: September 18, 1997 [Z 10942IE]
German version: *Angew. Chem.* **1998**, *110*, 649–651

Keywords: amino acids · CIDNP spectroscopy · NMR spectroscopy · photochemistry · radical ions

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[5] Scheme 1 shows the three types of radical cations derived from methionine (sulfur-centered radical cation Met-(S$^{\dot{+}}$), nitrogen-centered radical cation Met-(N$^{\dot{+}}$), and radical cation Met-(S$\overset{+}{\therefore}$N) with a two-center three-electron bond. The distribution of proton hyperfine coupling constants a in each radical is given schematically below the respective structural formula. Proton H^1 is attached to the carbon atom bearing the amino group (compare the formula in Figure 1).

[6] For simplicity, protonation equilibria are omitted in Scheme 1 and Figure 1; that is, methionine and its radical cations are displayed in their deprotonated forms, which is present above the respective pK_{a2} value. Because of H/D exchange with the solvent, the nitrogen atom bears no protons but only deuterons in our experiments.

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[10] Other experimental parameters: [CB] = 2×10^{-3} M, [Met] = 2×10^{-2} M, pH value adjusted by addition of KOH and measured with a glass electrode; room temperature, excitation wavelength 308 nm, 10 laser flashes per acquisition, 16 transients per spectrum. For details concerning the CIDNP setup, see ref. [1 f]. The method for background suppression is described in ref. [11].

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A Fully Encapsulated Acetylenediide in $Ag_2C_2\cdot8\,AgF$**

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Silver acetylide (silver carbide), Ag_2C_2, is highly explosive when dry, and violent decomposition occurs upon mechanical shock and on heating to 120–140 °C.[1] Several double salts of silver acetylide with other silver compounds are known,[2–4] but only silver acetylide/silver nitrate (1/6) has been structurally characterized.[5–6]

Up to now the linear structure **I** of silver acetylide (Figure 1) was inferred from its chemical properties, which are consistent with those of a molecular compound but differ greatly from those of the ionic carbides of Group 1 and 2

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[**] This work was supported by Hong Kong Research Grants Council Earmarked Grant CUHK 456/95P and Direct Grant A/C 2060090 of The Chinese University of Hong Kong.

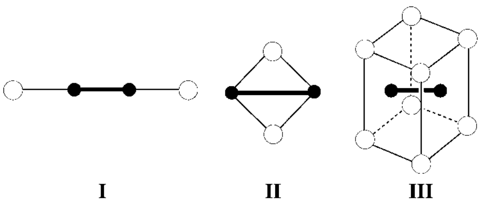

Figure 1. Modes for the coordination of the acetylenediide C_2^{2-} to metal atoms: end-on M_2C_2 (**I**), side-on M_2C_2 (**II**), and encapsulated in a metal cage $C_2@M_8$ (**III**).

elements, such as Na_2C_2 and CaC_2. Owing to the low solubility of silver acetylide, its crystal structure is unknown. However, the existence of a cationic $[C_2@Ag_8]$ cage moiety in $Ag_2C_2 \cdot 6\,AgNO_3$[6] implies that the C_2^{2-} group (acetylenediide, often referred to as the acetylide dianion) in silver acetylide prefers a double π-bridged (**II**) or fully encapsulated coordination mode (**III**), or is present as a mixture of linear and π-bridged structures to give a linear structure.

The double π-bridged structure **II** was postulated for the dilithioacetylene monomer Li_2C_2 on the basis of calculations,[7] and since then similar π interactions in polar alkali metal acetylides[8] and alkaline earth metal acetylides[9] have been studied and extensively discussed. Here we report the synthesis and characterization of $Ag_2C_2 \cdot 8\,AgF$, in which an acetylenediide is completely enclosed within the Ag_9 cage of a chandelierlike arrangement of ten silver atoms.

A single-crystal X-ray structure analysis of $Ag_2C_2 \cdot 8\,AgF$ showed the presence of an exohedral Ag atom attached to the apex of a cationic Ag_9 cage, whose cavity is filled by an undisordered acetylenediide, C_2^{2-} (Figure 2, top). The resulting $[C_2@Ag_9]Ag$ assembly has a twofold symmetry axis that passes through Ag1 and Ag2 and bisects the C≡C bond. The cationic Ag_9 cage can be described as a capped square antiprism of approximate C_{4v} symmetry from which all four edges of the expanded capped face have been removed. Hitherto the only known example of an analogous cluster is $[C_2@Ag_8]$ in $Ag_2C_2 \cdot 6\,AgNO_3$, in which eight Ag atoms form the vertices of a rhombohedron that completely encages the threefold disordered C_2^{2-} dianion.[6]

The Ag⋯Ag distances in the $[Ag_9]Ag$ framework range from 2.8441(4) to 3.0863(5) Å. They are comparable to the Ag⋯Ag distance of 2.89 Å in silver metal[10] and hence suggest the existence of weak Ag⋯Ag interactions of the same order of magnitude. There are three arrangements of fluoride ions around the six different silver centers. The atoms Ag1 and Ag2 are each bonded to four F atoms to form a tetragonal pyramid with Ag–F distances of 2.392(2)–2.471(2) Å; Ag3 and Ag4 each have two F neighbors at a distance of 2.196(2)–2.485(2) Å, and Ag5 and Ag6 each have three F neighbors at a distance of 2.299(2)–2.571(2) Å (Figure 2, bottom). Thus the crystal structure of $Ag_2C_2 \cdot 8\,AgF$ consists of a three-dimensional framework in which F atoms act as bridges between adjacent $[C_2@Ag_9]Ag$ moieties.

As shown in the bottom of Figure 2, the atom C1 forms three shorter bonds (represented by broken lines) with Ag3, Ag4, and Ag6. The bond lengths are 2.311(4), 2.247(4), and 2.110(4) Å, respectively. Notably, they are shorter and longer, respectively, than those of silver atoms π-bonded (average 2.452 Å) and σ-bonded (average 2.057 Å) to the C≡CR groups in the alkynyl complexes $[Ph_3PAgC{\equiv}CPh]_4 \cdot 3.5\,THF$ and $[Me_3PAgC{\equiv}CSiMe_3]_\infty$.[11] The bond angles between the enclosed acetylenediide and individual silver atoms (Ag-C1-C1A) are in the range of 116.2(4)–138.4(1)°, and are comparable to those between the C_2^{2-} species and "equatorial" Ag atoms in $Ag_2C_2 \cdot 6\,AgNO_3$.[6] The distance of 2.620(4) Å between the C_2^{2-} entity and "axial" atom Ag2 in the present compound is longer than the corresponding distances (2.45 and 2.56 Å) in $Ag_2C_2 \cdot 6\,AgNO_3$.[6] In contrast to the tetranuclear complex $[Cu_4(\mu\text{-dppm})_4(C{\equiv}C)][BF_4]_2$ (dppm = 1,2-bis(diphenylphosphanyl)methane),[12] in which the nearly coplanar bonding between the central C_2^{2-} ligand (C–C 1.26(2) Å) and peripheral Cu atoms allows a clear

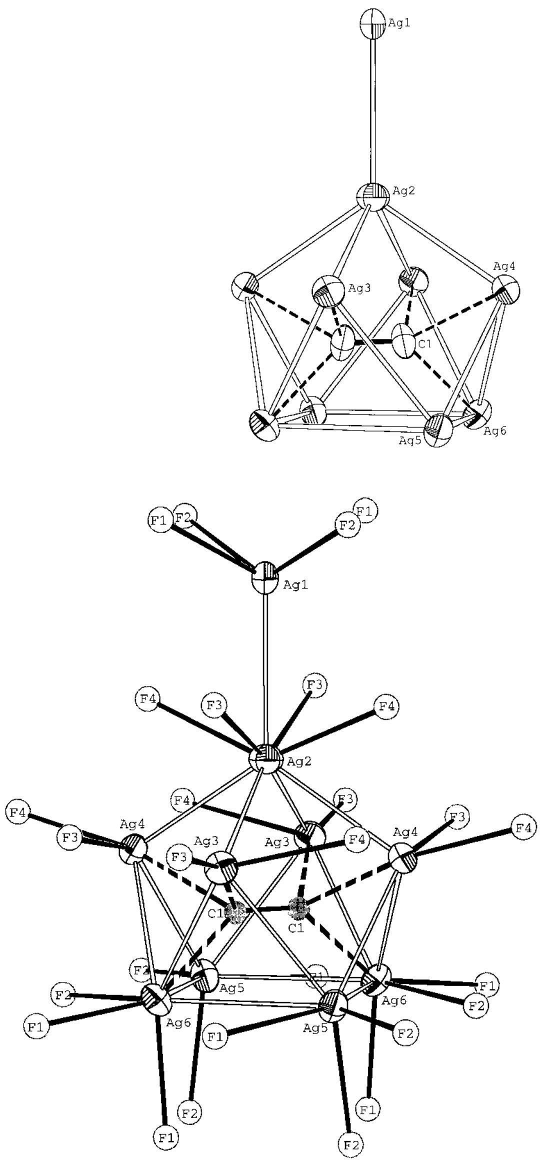

Figure 2. Crystal structure of $Ag_2C_2 \cdot 8\,AgF$. Top: chandelierlike $[Ag_9]Ag$ assembly accommodating a C_2^{2-} species in its cavity. The thermal ellipsoids are drawn at the 35 % probability level. Bottom: coordination environment of the individual silver atoms in the $[C_2@Ag_9]Ag$ moiety. Selected bond lengths [Å] and angles [°]: Ag3–C1 2.3114, Ag4–C1 2.2474, Ag5–C1 2.1104, C1–C1A 1.1757; C1-Ag2-C1A 25.92, Ag3-C1-C1A 116.24, Ag4-C1-C1A 122.84, Ag6-C1-C1A 138.41.

distinction to be made between σ and π coordination modes, the bonding interaction between the C_2^{2-} group and the cage Ag atoms in $Ag_2C_2\cdot 8\,AgF$ is ambiguous, as in the case of $Ag_2C_2\cdot 6\,AgNO_3$. In the complex $[(TiN_4Et_8)(C_2)(Li)_2(TiN_4Et_8)]^{2+}$ ($H_2N_4Et_8$ = *meso*-octaethylporphyrin), the sandwiched C_2 species is bonded to pairs of Ti and Li atoms in the end-on (**I**) and side-on (**II**) modes (see Figure 1), respectively, and has a C–C bond length of 1.30(1) Å.[13] The fully encapsulated coordination mode of the dicarbido group C_2^{n-} occurs in a number of transition metal clusters.[14] However, in many instances the C_2 unit can be considered to be formally derived from complete deprotonation of ethane ($n = 6$), ethylene ($n = 4$), or the vinylidene ligand ($n = 4$), as the C–C bond length generally lies between 1.32 and 1.60 Å.[15] The very short C1–C1A bond length of 1.175(7) Å in $Ag_2C_2\cdot 8\,AgF$ is comparable to that of acetylene (1.205 Å) and indicates that the encapsulated acetylenediide retains the triple-bond character of the starting material silver acetylide, as was confirmed by laser Raman spectroscopy (see Experimental Section). Molecular orbital calculations on ethanido clusters indicated that the C_2 entity enters into a synergic bonding interaction with the skeletal molecular orbitals of the metal cage, and the C–C bond length correlates with the degree of metal-to-ligand backbonding.[16] A similar molecular orbital picture may account for stabilization of the highly explosive silver acetylide by trapping the acetylide dianion inside a variety of polyhedral metal cages through formation of silver(I) double salts.

Experimental Section

Ag_2C_2: A slow stream of acetylene gas was bubbled into a stirred aqueous solution of silver nitrate at room temperature until saturation was reached. The white precipitate of Ag_2C_2 was isolated by filtration, washed several times with deionized water, and temporarily stored in wet form in the dark. **Caution**: Ag_2C_2 should never be dried or kept for a prolonged period, and only a small quantity should be used in any chemical reaction.

Moist Ag_2C_2 was added to 2 mL of a concentrated aqueous solution of AgF (about 40%) in a plastic vessel with stirring until saturated. The excess of Ag_2C_2 was filtered off, and the solution was placed in a desiccator charged with P_2O_5. In the course of two days colorless crystals of $Ag_2C_2\cdot 8\,AgF$ were obtained. The laser Raman spectrum of this crystalline product, as measured on a Renishaw Raman Image Microscope System 2000, exhibits a doublet of about equal intensity at 2104.5 and 2168.6 cm^{-1} in the $\Delta\nu(C{\equiv}C)$ region, which arises from Fermi resonance between the stretching vibration of C_2^{2-} and the first overtone of the laser excitation line at 1125.3 cm^{-1}.

Crystal structure analysis: A colorless crystal of dimensions 0.03 × 0.03 × 0.04 mm was mounted in a 0.3 mm Lindemann glass capillary and used for data collection on a Rigaku RAXIS IIC imaging plate diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator powered at 50 kV and 90 mA. Thirty-one oscillation frames were recorded in the range of $\phi = 0-180°$ with $\Delta\phi = 5.0°$ and 8 min exposure per frame. Crystal data for $Ag_2C_2\cdot 8\,AgF$: $M_r = 1254.7$, tetragonal, space group $P\bar{4}$ (no. 81), $a = 7.464(1)$, $c = 10.337(1)$ Å, $V = 575.9(1)$ Å^3, $T = 293$ K, $Z = 2$, $\rho_{calcd} = 7.236$ g cm^{-3}, $F(000) = 1108$, $\mu(Mo_{K\alpha}) = 166.82$ cm^{-1}, absorption corrections applied by using ABSCOR, relative transmission factors in the range 0.788–1.0. A total of 1888 reflections were collected in the 2θ range 4.0–52.0° ($-9 \le h \le 9$, $0 \le k \le 9$, $-12 \le l \le 12$) and led to 1040 unique reflections ($R_{int} = 5.05\%$), 988 of which with $I > 2\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined by full-matrix least squares on F^2 by using the Siemens SHELXTL/PC package of crystallographic software.[17] All non-hydrogen atoms were refined anisotropically. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407646.

Received: September 26, 1997
Revised version: November 7, 1997 [Z10976IE]
German version: *Angew. Chem.* **1998**, *110*, 652–654

Keywords: acetylene · carbides · clusters · fluorine · silver

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