

Reconfirmation of Solubility of C_2^{2-} in Liquid Ammonia: Syntheses and Crystal Structures of the Tetrahedral Acetylide Ammoniates $[Zn(C_2H)_4]^{2-}$, $[Cd(C_2H)_4]^{2-}$ and $[In(C_6H_5)_3(C_2H)]^-$

Marina Kaas^{+, [b]}, Melanie Werker^{+, [a]}, Nikolaus Korber^{*, [b]} and Uwe Ruschewitz^{*, [a]}

Dedicated to Prof. Dr. Josef Breu on the occasion of his 60th birthday

The new compounds with the sum formulae $[Cs([18]crown-6)]_2[Zn(C_2H)_4] \cdot 8NH_3$, $Rb_3[Rb([18]crown-6)(NH_3)][Cd(C_2H)_4]_2 \cdot \{[18]crown-6 \cdot 2NH_3\} \cdot NH_3$ and $[Cs([2.2.2]crypt)][In(C_6H_5)_3(C_2H)]$ were synthesized in liquid ammonia. The anionic units show tetrahedrally coordinated central atoms with four hydrogenacetylide ligands or one C_2H^- and three $C_6H_5^-$ ligands. Solid state starting materials for these ligands were either AC_2H ($A=Rb, Cs$) or Cs_2C_2 . The fact that the indium compound contains a hydrogenacetylide ligand, which was formed from Cs_2C_2 , confirms again the equilibrium of the species C_2H_2 , C_2H^- and C_2^{2-} in liquid ammonia and again proves that acetylides slowly dissolve in this medium.

compounds have been obtained in polycrystalline form and were structurally characterized in detail predominantly via x-ray powder diffraction experiments.^[2] In general these compounds are insoluble in common solvents.^[3] However, during the synthesis of $KCuC_2$ a possible solubility of the acetylides in liquid ammonia was observed for the first time. A suspension of potassium acetylide and copper iodide reacts at low temperatures of $-78^\circ C$ within minutes to yield $KCuC_2$.^[4] Based on this observation, the solubility of acetylides in liquid ammonia was investigated in more detail. By dissolving the acetylides K_2C_2 , Rb_2C_2 and Cs_2C_2 in liquid ammonia, it was possible to obtain single crystals of these acetylides as ammoniates with the compositions $K_2C_2 \cdot 2NH_3$, $Rb_2C_2 \cdot 2NH_3$ and $Cs_2C_2 \cdot 7NH_3$. Additionally, an equilibrium between acetylene, hydrogenacetylide and acetylide in liquid ammonia was postulated because also the crystallization of $[Li(NH_3)_4]C_2H$ was observed. The hydrogenacetylide anion C_2H^- in the compound was formed in solution from the starting material Li_2C_2 .^[5] In addition to the already mentioned ternary alkali metal copper acetylides,^[4] many ternary alkali metal transition metal acetylides have been reported for d^{10} configured metals like $Pd(0)$,^[6,7,8] $Pt(0)$,^[6,7,8] $Ag(I)$ ^[9] and $Au(I)$.^[10] All of them show a linear coordination of the d^{10} metal by end-on bound acetylide anions leading to chain-type structural fragments.^[11] Extending the central atoms to $Zn(II)$ or $Cd(II)$ a tetrahedral coordination sphere and the formation of 3D networks seemed to be conceivable. Recently a compound of the composition $Cs_2Cd(C_2H)_2(C_2)$ has been presented. This compound is synthesized from caesium tetraethynylcadmate^[12] via two different routes – on the one hand by heating to $200^\circ C$ in an argon atmosphere and on the other hand under ammonothermal conditions.^[13] The starting material $Cs_2Cd(C_2H)_4$ and its analogues^[12,14,15,16] are well-known and contain isolated $[M^II(C_2H)_4]^{2-}$ tetrahedra. Usually they can only be obtained in polycrystalline form but some ammoniates of the potassium compounds^[17] ($K_2Cd(C_2H)_4 \cdot 2NH_3$ and $K_2Zn(C_2H)_4 \cdot 2NH_3$) were obtained as single crystals indicating a good solubility in liquid ammonia. $Cs_2Cd(C_2H)_2(C_2)$ contains terminating C_2H^- as well as bridging C_2^{2-} ions and shows a new structural design of the type $[M^II(C_2H)_{2/1}(C_2)_{2/2}]^{2-}$. This compound represents an intermediate on the way to a fully bridged 3D acetylide.^[13]

At this point, our research focused on the crystallization of further ammoniates of (hydrogen-) acetylides, with and without

Introduction

Based on the excellent work of the french chemist and nobel prize winner H. Moissan, alkali metal acetylides have been well-known for more than 100 years. In a first step, he synthesized alkali metal hydrogenacetylides by reacting alkali metals dissolved in liquid ammonia with acetylene. In a second step, hydrogenacetylides were then converted into the corresponding alkali metal acetylides by heating in vacuo.^[1] These

[a] Dr. M. Werker,⁺ Prof. Dr. U. Ruschewitz
Institute of Inorganic Chemistry, Department of Chemistry
University of Cologne
GreinstraÙe 6
D-50939 Cologne, Germany
E-mail: uwe.ruschewitz@uni-koeln.de

[b] Dr. M. Kaas,⁺ Prof. Dr. N. Korber
Institute of Inorganic Chemistry
Universität Regensburg
Universitätstraße 31
93051 Regensburg, Germany
E-mail: nikolaus.korber@chemie.uni-regensburg.de

[⁺] These authors contributed equally to this work.

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chelating reagents. In the following, we will present some of our results.

Results and Discussion

All three compounds with the sum formulae $[\text{Cs}(\text{[18]crown-6})]_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 8\text{NH}_3$, $\text{Rb}_3[\text{Rb}(\text{[18]crown-6})(\text{NH}_3)]_2[\text{Cd}(\text{C}_2\text{H})_4] \cdot \{\text{[18]crown-6} \cdot 2\text{NH}_3\} \cdot \text{NH}_3$ and $[\text{Cs}(\text{[2.2.2]crypt})][\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]$ show as their anionic units a tetrahedrally coordinated central atom with either four hydrogenacetylide ligands or in case of the indium species one C_2H^- and three C_6H_5^- ligands. The $M(\text{C}_2\text{H})_4$ units exhibit an overall charge of $2-$, which is the result of four onefold negatively charged hydrogenacetylide ligands and a Zn^{2+} or Cd^{2+} central atom. In contrast to that, the $[\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]$ unit shows a total charge of $1-$, which can be explained by one negatively charged C_2H^- , three C_6H_5^- ligands and a central In^{3+} cation. As given in the sum formulae, charge neutrality is achieved by alkali metal cations which are either chelated by agents like [18]-crown-6 (= 1,4,7,10,13,16-hexaoxacyclooctadecane) or [2.2.2]crypt (= 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) or spherically saturated by ammonia molecules and/or hydrogenacetylide ligands.

$[\text{Zn}(\text{C}_2\text{H})_4]^{2-}$ and $[\text{Cd}(\text{C}_2\text{H})_4]^{2-}$

$[\text{Cs}(\text{[18]crown-6})]_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 8\text{NH}_3$ crystallizes in the orthorhombic space group $Pmmn$ and contains 0.25 formula units in the asymmetric unit. Some atoms are located on general Wyckoff positions and logical fragments are generated by symmetry operations. For a detailed description please check the supporting information. The anionic component thus results in a $[\text{Zn}(\text{C}_2\text{H})_4]^{2-}$ molecular anion, built by a central Zn atom in the formal oxidation state $+II$, which is surrounded by four onefold negatively charged hydrogenacetylide ligands in a nearly ideal tetrahedral coordination. The distortions within the polyhedron were calculated using the Continuous Shape Measures (CSHM) approach by Llunell et al.^[18] A low CSHM_{T-4} value of 0.117 for the ZnC_4 polyhedron points to a tetrahedron with only small distortions. Selected distances and angles are given in Table 1. The average C–C distance is 1.19 Å and matches with the expected value for carbon triple bonds.^[19] The distances between C2–H2 and C4–H4 are in the expected range of typical C–H-bonds taking the standard deviations into account. All other geometric parameters are in good agreement with values reported for the compounds $\text{K}_2\text{Zn}(\text{C}_2\text{H})_4 \cdot 2\text{NH}_3$ and $\text{Rb}_2\text{Zn}(\text{C}_2\text{H})_4$.^[17,12] The overall negative charge of $2-$ is compensated by two $[\text{Cs}(\text{[18]crown-6})]$ cation complexes, which are identical generated by symmetry. The chelate molecule shows rotational disorder which can be modelled by splitting atoms and adding different occupation factors (for values see table S1.7 in the SI). These operations lead to three different orientations of the crown ether molecule (see Figure S1.2 in the SI) of which only few H atoms could be refined. The Cs atom is lifted out of the imaginary oxygen plane and is η^2 -coordinated in the same direction by three hydrogenacetylide ligands of

Table 1. Interatomic distances [Å] of the C_2H^- ligands in the tetrahedral anions. More geometric parameters are given in the supporting material.

Atoms	$[\text{Zn}(\text{C}_2\text{H})_4]^{2-}$	$[\text{Cd}(\text{C}_2\text{H})_4]^{2-}$	$[\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]^-$
M1–C1	2.024(14), 2x	2.257(7), 3x	2.179(6)
M1–C3	2.071(15), 2x	2.204(11)	
M2–C5		2.258(6), 3x	
M2–C7		2.199(11)	
C1–C2	1.206(19)	1.211(10)	1.191(9)
C3–C4	1.18(2)	1.207(18)	
C5–C6		1.194(10)	
C7–C8		1.178(19)	
C2–H2	1.07(10)	1.00(2)	0.93
C4–H4	1.24(12)	1.06(15)	
C6–H6		1.00(2)	
C8–H8		0.93	

one anionic unit (see figure 1). The coordination sphere of the Cs cation is saturated by one ammonia molecule of solvation. Three further solvent molecules are found in the unit cell, of which one N atom shows a very large thermal ellipsoid (see Figure S1.3 in the SI). Its position in the cell leads to a cluster of only partially occupied atoms.

The anionic component of the Cd species shows the same structural motif as the Zn compound: A tetrahedrally coordinated central atom in the formal oxidation state $+II$ and four hydrogenacetylide ligands. Apart from that $\text{Rb}_3[\text{Rb}(\text{[18]crown-6})(\text{NH}_3)]_2[\text{Cd}(\text{C}_2\text{H})_4] \cdot \{\text{[18]crown-6} \cdot 2\text{NH}_3\} \cdot \text{NH}_3$ crystallizes in the higher symmetric rhombohedral space group $R\bar{3}m$ and consequently the asymmetric unit only contains 1/6 formula units. In the supporting material an overview of the occupied Wyckoff positions is given. One striking feature of the structure is the very long c-axis (see Figure S2.3 in the SI), leading to a diffraction pattern with reflections, which are very close to each another in this direction (see Figure S2.4 in the SI). Furthermore, there are two symmetrically independent $[\text{Cd}(\text{C}_2\text{H})_4]^{2-}$ units in the unit cell with slightly different geometries.

The values from Shape^[18] are 0.024 for the polyhedron around Cd1 and 0.067 for the polyhedron around Cd2, which

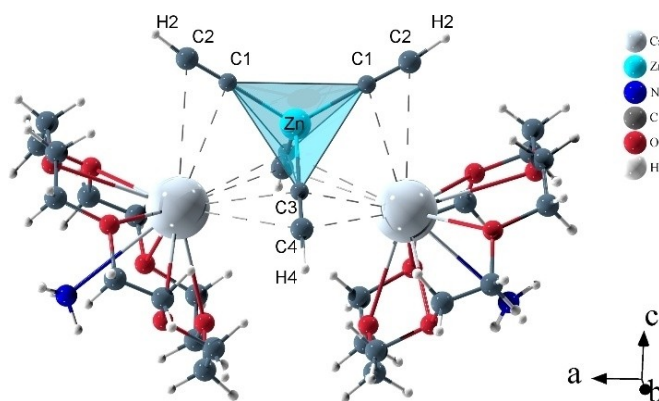


Figure 1. The tetrahedral $[\text{Zn}(\text{C}_2\text{H})_4]^{2-}$ anion with two $[\text{Cs}(\text{[18]crown-6})]^+$ cation complexes in $[\text{Cs}(\text{[18]crown-6})]_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 8\text{NH}_3$.

point to an only very weak distortion of the tetrahedrons. This (trigonal) distortion is also reflected in the different Cd–C distances in both symmetrically independent anions (cp. Table 1): the Cd–C distance along the three-fold axis of the tetrahedron is always slightly shorter ($\sim 0.05\text{--}0.06\text{ \AA}$) than the three other Cd–C distances. It is notable that the three-fold axes of the tetrahedrons are parallel to the long *c*-axis. Besides this, the tetrahedrons are disordered, which was modelled with a second set of Cd atoms named Cd1A and Cd2A (see Figure S2.5 in the SI, occupancy factors are around 0.05 for Cd1A and 0.02 for Cd2A). The associated lighter atoms could not be refined. Apart from that, the average Cd–C distance of 2.23 \AA is in good agreement with the corresponding values in $\text{K}_2\text{Cd}(\text{C}_2\text{H})_4 \cdot 2\text{NH}_3$ and $\text{Rb}_2\text{Cd}(\text{C}_2\text{H})_4$.^[17,12] The C–C distances are in the expected range of carbon triple bonds.^[19] For further geometric parameters please check Table 1 and the supporting material. The overall negative charge of both anionic units ($2 \times 2-$) is compensated by one [Rb([18]crown-6)] cation complex (named Rb2) and three Rb cations (named Rb1). The coordination sphere of Rb2 consists of three η^2 -coordinations to hydrogenacetylide ligands and the contact to one ammonia molecule through the crown ether molecule and is similar to the coordination sphere of the Cs1 atom in $[\text{Cs}([18]\text{crown-6})]_2[\text{Zn}(\text{C}_2\text{H})_4] \cdot 8\text{NH}_3$. The coordination spheres of the Rb1 cations are saturated by η^2 -contacts to four hydrogenacetylide ligands of two different anions as well as to two oxygen atoms of two different crown ether molecules (see figures 2 and S2.2 in the SI). One of the [18]crown-6 molecules binds NH_3 on both sides of the carbon oxygen ring. The arrangement of anionic and cationic fragments leads to a layer-type structure of $[\text{Cd}(\text{C}_2\text{H})_4]_n \cdots \text{Rb1}$ units parallel to (001). Furthermore, the structure includes one unattached solvent molecule.

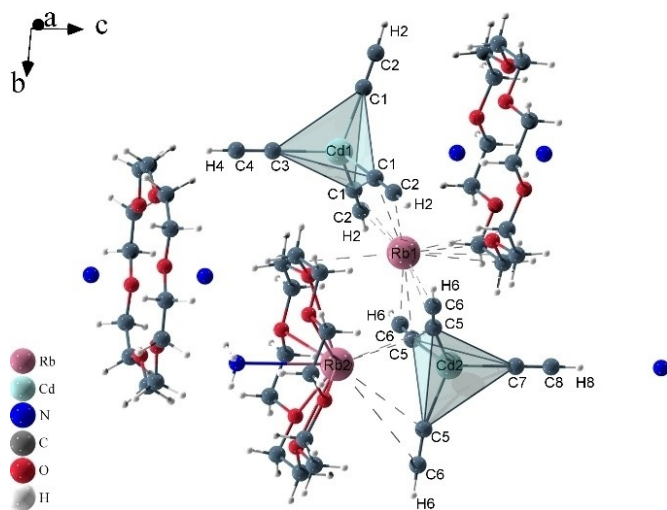


Figure 2. The two symmetrically inequivalent $[\text{Cd}(\text{C}_2\text{H})_4]^{2-}$ anions with their surroundings in the structure of $\text{Rb}_3[\text{Rb}([18]\text{crown-6})(\text{NH}_3)][\text{Cd}(\text{C}_2\text{H})_4]_2 \cdot \{ [18]\text{crown-6} \cdot 2\text{NH}_3 \} \cdot \text{NH}_3$.

$[\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]^-$

The indium compound differs from the above-mentioned Zn and Cd species not just because it crystallizes in the monoclinic space group $P2_1/n$ but also because the central atom is surrounded by only one negatively charged hydrogenacetylide and three phenyl ligands (see Figure 3). Taking the number of counter cations per formula unit into account the oxidation state of the indium atom is assigned to +III. The In–C bonds can be divided into the longer In–(C_6H_5) and the slightly shorter In–(C_2H) distances. The latter matches with the value found in $[\text{Li}(\text{thf})_4][\text{In}(\text{C}_2(\text{C}_6\text{H}_5))_4]$ (thf = tetrahydrofuran).^[20] In accordance with typical values for carbon triple bonds the C–C distance in the hydrogenacetylide ligand is $1.191(10)\text{ \AA}$.^[19] The spatial positions of the four carbon atoms attached to the central indium atom result in a nearly perfect tetrahedron. The calculation with Shape yields in a low $\text{CSH}_{\text{M}-4}$ value of 0.071 and points to a very slight distortion.^[18] Charge neutrality in the compound is achieved by a Cs cation which is chelated by a [2.2.2]crypt molecule.

Probably the most notable difference from the group 12 compounds is the fact that the indium species was synthesized by using the dialkali metal acetylide Cs_2C_2 as starting material. For the Zn and Cd compounds the hydrogenacetylides RbC_2H and CsC_2H were used as starting materials. In our earlier publication we described the equilibrium between the acetylide species H_2C_2 , C_2H^- and C_2^{2-} in liquid ammonia and that acetylide solids slowly dissolve in this medium.^[5] With these new results, we can now reconfirm that the C_2^{2-} dumbbell in Cs_2C_2 is protonated to the HC_2^- species in liquid ammonia (see Scheme 1). The hydrogenacetylide unit then reacts with suitable central atoms in complexes or organometallic compounds and can replace weaker bonded ligands. Previously used starting materials like $\text{A}_2\text{Zn}(\text{CN})_4$ ($\text{A} = \text{alkali metal}$), $[\text{Zn}(\text{NH}_3)_2](\text{SCN})_2$ or $\text{Cd}(\text{SCN})_2$ were suitable for the synthesis of tetraethynylzincates or -cadmat as well but did not always lead to crystalline products.^[12]

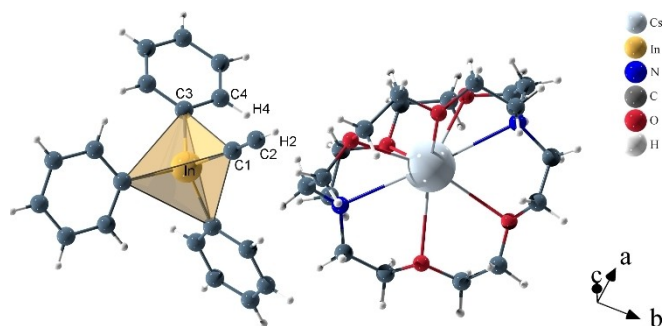


Figure 3. The asymmetric unit in $[\text{Cs}([2.2.2]\text{crypt})][\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]$ with the $[\text{In}(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H})]^-$ tetrahedron.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acetylides · crystal structure · hydrogenacetylide ligand · liquid ammonia · tetrahedral anions

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