Inorg. Chem. **2003**, *42*, 7716–7718

Inorganic Chemistry
Communication

The Diammoniates of Dipotassiumtetraethinylozincate and -cadmate: $K_2M(C_2H)_4{\cdot}2NH_3$ (M = Zn, Cd)

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Received June 6, 2003

By reaction of KC_2H and $K_2Zn(CN)_4$ in liquid ammonia, the diammoniate $K_2Zn(C_2H)_4{\cdot}2NH_3$ was obtained. $K_2Cd(C_2H)_4{\cdot}2NH_3$ was synthesized by reacting KC_2H, $Cd(NH_2)_2$, and acetylene in liquid ammonia. The crystal structures of the air and temperature sensitive compounds were determined by X-ray single crystal diffraction at low temperatures (T = 170 K). Both compounds crystallize in the monoclinic space group $I2/a$ (No. 15) with Z = 4. $K_2Zn(C_2H)_4{\cdot}2NH_3$: a = 7.289(1) Å, b = 12.765(2) Å, c = 14.066(2) Å, β = 98.11(2)°. $K_2Cd(C_2H)_4{\cdot}2NH_3$: a = 7.444(1) Å, b = 12.619(3) Å, c = 14.304(2) Å, β = 98.94(1)°. Characteristic structural motifs are tetrahedral $[M(C_2H)_4]^{2-}$ fragments (M = Zn, Cd) and zigzag chains of edge sharing distorted $(C_2H)_6$ octahedra centered by potassium ions. These zigzag chains are connected by a second type of crystallographically distinct potassium ions that also bind to two ammonia molecules.

We are interested in the synthesis and characterization of ternary transition metal acetylides of general composition $A_xM(C_2)_y$ (A = alkali metal, M = transition metal),[1−5] as they are promising model compounds on the border between metallic and saltlike behavior: Na_2PdC_2 [3] is black and a semiconductor with a small indirect band gap, whereas colorless $KAgC_2$ [5] shows insulating properties. For the synthesis of the latter compound, we used a generally applicable synthetic route, in which alkali metal hydrogen acetylides are reacted with metal iodides in liquid ammonia leading to precursors, which can be converted to the requested acetylides by heating in a vacuum. Although none of the intermediates could be isolated and characterized, the following reaction scheme seems to be likely:

$$2AC_2H + MI \xrightarrow{NH_3(l)} A[M(C_2H)_2] + AI$$

$$A[M(C_2H)_2] \xrightarrow{\Delta} AMC_2 + C_2H_2$$

with A = alkali metal, M = Ag,[5] Au.[4]

In this context, we are interested in alkali metal tetraethinylozincates and -cadmates as they could be useful precursors for the synthesis of ternary alkali metal zinc/cadmium acetylides, which are unknown up to now. Their synthesis in liquid ammonia has already been described,[6,7] and the crystal structures of $K_2M^{II}(C_2H)_4$ (M^{II} = Zn, Cd) were solved and refined from X-ray powder diffraction data.[8] They are isotypic ($I4_1/a$, Z = 4) and consist of isolated $[M^{II}(C_2H)_4]^{2-}$ tetrahedra, which are separated by the potassium ions.

For the synthesis of $K_2Zn(C_2H)_4$, $K_2Zn(CN)_4$ is reacted with KC_2H in liquid ammonia, which leads to a polycrystalline precipitate.[6]

$$4KC_2H + K_2Zn(CN)_4 \xrightarrow{NH_3(l)} K_2Zn(C_2H)_4 + 4KCN$$

For the respective cadmate $K_2Cd(C_2H)_4$, an analogous synthesis using $K_2Cd(CN)_4$ is not applicable, as $K_2Cd(C_2H)_4$ is very soluble in liquid ammonia so that after evaporation of most of the solvent a product containing KCN as an impurity is obtained. Therefore, $Cd(NH_2)_2$ is reacted with KC_2H and acetylene, which leads to no byproducts after complete evaporation of the ammonia.[7]

$$2KC_2H + Cd(NH_2)_2 + 2C_2H_2 \xrightarrow{NH_3(l)} K_2Cd(C_2H)_4 + 2NH_3$$

When trying to reproduce these syntheses, we found that in the case of the zinc compound colorless transparent crystals with a well-defined habit could be obtained after cooling at 195 K in liquid ammonia overnight. In the case of the cadmate, corresponding single crystals grew after evaporation of most of the ammonia and cooling at 195 K for some minutes. But after warming to ambient temperature, these crystals became dull and their diffraction patterns only showed Debye rings on an X-ray single crystal diffractometer. Thus, the

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10.1021/ic034629p CCC: $25.00

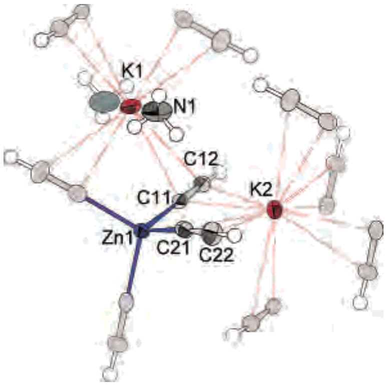

Figure 1. ORTEP diagram of the molecular structure of $K_2Zn(C_2H)_4\cdot 2NH_3$ showing 50% probability thermal ellipsoids and the atom-numbering scheme. Selected interatomic distances (Å) are Zn(1)−C(11) 2.051(3), Zn(1)−C(21) 2.056(3), C(11)−C(12) 1.203(4), C(21)−C(22) 1.202(5), K(1)−N(1) 2.952(4), K(1)−C 2.997(3)−3.276(3), K(2)−C 3.000(3)−3.291(3).

removal of the ammonia led to the formation of a polycrystalline material, although the habit of the crystals did not change during this procedure. Therefore, we isolated single crystals at temperatures below 243 K using a well-established technique.[9] These crystals[10] were analyzed on an X-ray single crystal diffractometer at 170(2) K, which revealed that the diammoniates of the tetraethinylometalates described in the literature were obtained.[6−8]

The results of the X-ray single crystal structure analysis of $K_2Zn(C_2H)_4\cdot 2NH_3$ [11] are presented in Figure 1. Zn is coordinated tetrahedrally by four C_2H^- groups, which are σ-bonded via the negatively charged carbon atom. The bonding angles C−Zn−C are in the range 105.8(1)−116.9(2)° pointing to a slightly distorted tetrahedron due to the influence of the ammonia molecules in the second coordination sphere. In the ammonia free compound $K_2Zn(C_2H)_4$, a less distorted $Zn(C_2H)_4$ tetrahedron was found.[8] The Zn−C−C unit in the diammoniate is almost linear (Zn(1)−C(11)−C(12) 179.2(2)°, Zn(1)−C(21)−C(22) 171.8(3)°). C−C distances of 1.203 and 1.202 Å in the C_2H ligand are in good agreement with the value expected for a C−C triple bond.[12] K(1) is coordinated octahedrally by four C_2H dumbbells in a side-on fashion and two ammonia molecules in trans positions. The resulting K−N and K−C distances compare well with those found in KNH_2 (2.875−3.307 Å)[13] and K_2C_2 (3.009−3.146 Å).[14] K(2) is coordinated octahedrally by six C_2H units in a side-on fashion with similar K−C distances. Side-on coordinated C_2H units are also found in KC_2H, where K is surrounded by five C_2H units, four in a side-on (K−C: 3.048 Å, 4×; 3.270 Å, 4×) and one in an end-on coordination mode (K−C: 2.876 Å).[15]

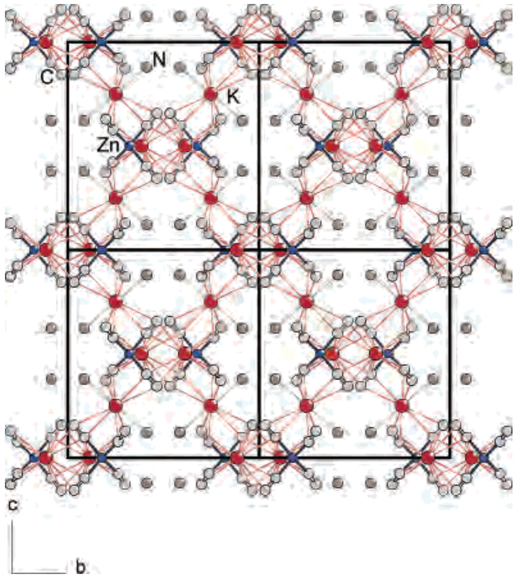

Figure 2. Packing diagram of $K_2Zn(C_2H)_4\cdot 2NH_3$ in a projection along [100]. Four unit cells are shown, hydrogen atoms have been omitted for clarity.

Analogous results were obtained for the crystal structure of $K_2Cd(C_2H)_4\cdot 2NH_3$.[16] Some selected distances (Å) are Cd(1)−C(11) 2.232(3), Cd(1)−C(21) 2.247(3), C(11)−C(12) 1.197(5), C(21)−C(22) 1.183(5), K(1)−N(1) 2.956(4), K(1)−C 3.023(3)−3.343(5), and K(2)−C 3.010(3)−3.375(4). The C−Cd−C angles in the $Cd(C_2H)_4$ tetrahedron are in the range 105.4(1)−118.8(2)° pointing to a stronger distortion from ideal symmetry in the cadmate. The Cd−C−C unit is again close to linear (Cd(1)−C(11)−C(12) 179.1(3)°, Cd(1)−C(21)−C(22) 170.3(3)°).

In Figure 2, the packing diagram of the crystal structure of $K_2Zn(C_2H)_4\cdot 2NH_3$ is shown. K(2) centered $(C_2H)_6$ octa-

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(10) Single crystals of $K_2Zn(C_2H)_4\cdot 2NH_3$ and $K_2Cd(C_2H)_4\cdot 2NH_3$ were obtained by following the procedures given in the literature[6,7] and cooling procedures given in the text. But instead of removing the ammonia by heating, the precipitated crystals were transferred with a cooled spatula to a precooled inert oil (Galden HT 90, Ausimont S.p.A.). Using a well-established low temperature device,[9] single crystals suitable for X-ray structure analysis were selected under a polarizing microscope, mounted in glass capillaries, and frozen in liquid nitrogen prior to the measurements. Additionally, the crystallographic data for the crystal structures of $K_2Zn(C_2H)_4\cdot 2NH_3$ and $K_2Cd(C_2H)_4\cdot 2NH_3$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-212153 and CCDC-212154, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

(11) A single crystal of $K_2Zn(C_2H)_4\cdot 2NH_3$ sealed in a glass capillary and frozen in liquid nitrogen was mounted on a precooled (170(2) K) STOE image-plate diffractometer (IPDS I, graphite-monochromatized Mo Kα radiation) collecting 1024 independent reflections (R(int) = 0.0683), of which 821 reflections were observed with $I > 2\sigma(I)$. Crystal data: monoclinic, space group $I2/a$, $a = 7.289(1)$ Å, $b = 12.765(2)$ Å, $c = 14.066(2)$ Å, $\beta = 98.11(2)°$, $Z = 4$. The structure was solved by direct methods (SHELXS-97) and subsequent difference Fourier syntheses, in which all hydrogen atoms were found. Full-matrix least-squares refinements on F^2 (SHELXL-93) using anisotropic thermal parameters for all non-hydrogen atoms led to R1 = 0.0233 and wR2 = 0.0502 for $I > 2\sigma(I)$.

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(16) A single crystal of $K_2Cd(C_2H)_4\cdot 2NH_3$ sealed in a glass capillary and frozen in liquid nitrogen was mounted on a precooled (170(2) K) STOE image-plate diffractometer (IPDS II, graphite-monochromatized Mo Kα radiation) collecting 1261 independent reflections (R(int) = 0.0700), of which 1060 reflections were observed with $I > 2\sigma(I)$. Crystal data: monoclinic, space group $I2/a$, $a = 7.444(1)$ Å, $b = 12.619(3)$ Å, $c = 14.304(2)$ Å, $\beta = 98.94(1)°$, $Z = 4$. The structure was solved by direct methods (SHELXS-97) and subsequent difference Fourier syntheses, in which all hydrogen atoms were found. Full-matrix least-squares refinements on F^2 (SHELXL-93) using anisotropic thermal parameters for all non-hydrogen atoms led to R1 = 0.0221 and wR2 = 0.0376 for $I > 2\sigma(I)$.

hedra are connected by common edges to form zigzag chains running parallel to [100]. These zigzag chains are interconnected by K(1) centered $(C_2H)_4(NH_3)_2$ octahedra so that a three-dimensional framework results. The ammonia molecules reside in channels parallel to [100], which are formed by the connected KR_6 octahedra ($R = C_2H^-$, NH_3). As the connection only involves C_2H^- units, the ammonia molecules occupy terminal positions. This aspect is quite obvious from Figure 2. It can now be assumed that the ammonia molecules are able to leave crystals of $K_2M(C_2H)_4{\cdot}2NH_3$ (M = Zn, Cd) along the channels running parallel to [100]. This could explain that the crystal habit remains almost unchanged on heating, but the color change and the occurrence of Debye rings indicate that some structural rearrangements must have taken place inside the crystals so that a polycrystalline material results.

Up to now, all our attempts to synthesize more examples for ammoniates of ethinylometalates of composition $A_xM(C_2H)_y{\cdot}zNH_3$ (A = alkali and alkaline earth metals, M = Zn, Cd, Mn, Cu) have been hampered by their high thermal and oxidation sensitivity, which even exceeds the instability of the title compounds.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Supporting Information Available: Crystallographic data in CIF format for the compounds $K_2Zn(C_2H)_4{\cdot}2NH_3$ and $K_2Cd(C_2H)_4{\cdot}2NH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034629P