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Transformation of Ammonium Dicyanamide into Dicyandiamide in the Solid

Barbara Jürgens, Henning A. Höppe, Elisabeth Irran, and Wolfgang Schnick*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (D),
D-81377 München, Germany

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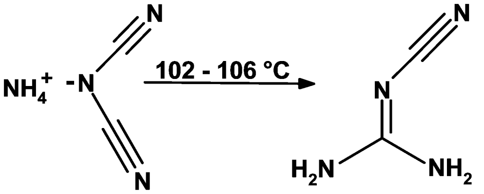
Ammonium dicyanamide $NH_4[N(CN)_2]$ was synthesized through aqueous ion exchange. The crystal structure was investigated by single-crystal X-ray diffraction ($P2_1/c$, $a = 378.67(6)$ pm, $b = 1240.9(3)$ pm, $c = 911.84(14)$ pm, $\beta = 91.488(18)°$, $Z = 4$). It derives from the CsCl structure type. Medium strong hydrogen bonds between NH_4^+ and $[N(CN)_2]^-$ ions are indicative of the observed formation of dicyandiamide $H_4C_2N_4$ during heating. According to DSC and temperature-dependent X-ray powder diffractometry, this isomerization is exothermic and occurs between 102 and 106 °C in the solid. The reaction represents the isolobal analogue to the classical synthesis of urea by heating NH_4OCN. While other alkali and alkaline earth dicyanamides undergo trimerization or polymerization of their anions during heating, ammonium dicyanamide thus shows a different reactivity.

In the past few years the transition metal dicyanamides $M^{II}[N(CN)_2]_2$ (M^{II} = Cr, Mn, Fe, Co, Ni, Cu) and coordination compounds containing $[N(CN)_2]^-$ ligands were investigated in detail because of their potential use as molecular magnets.[1−3]

Apart from this feature the thermal behavior of simple ionic dicyanamides was investigated. The occurring phase transitions were studied, and the varying reactivity of the dicyanamide ion was correlated with the cations involved: During heating the anions of the alkali dicyanamides $M[N(CN)_2]$ trimerize, forming the cyclic tricyanomelaminates $M_3[C_6N_9]$. Depending on the cation this reaction occurs in the solid (M = Na)[4] or in the melt (M = K,[5] Rb,[5] Cs[6]), respectively. For lithium dicyanamide a similar oligomerization of the anions or even a polymerization to products of hitherto unknown structure has been discussed.[7]

In contrast to the alkali dicyanamides the respective alkaline earth salts (M^{II} = Mg, Ca, Sr, Ba)[8] as well as the dicyanamides of other divalent metals (M^{II} = Co and Ni,[9] Zn,[10] Pb[11]) do not show formation of the respective tricyanomelaminates $M^{II}_3[C_6N_9]_2$. During thermolysis these salts form X-ray amorphous products and the FTIR spectra show broad signals indicating a further polymerization of the dicyanamide ions.

With regard to the reactivity of the dicyanamide ion depending on the cation as mentioned above, the thermal behavior of ammonium dicyanamide caught our interest. In the literature the synthesis of ammonium dicyanamide $NH_4[N(CN)_2]$ and its IR and NMR spectra were mentioned, but structural data have not been reported as yet.[12−14] Disagreeing information was available about the thermal behavior of $NH_4[N(CN)_2]$: Madelung et al. reported a melting point of 116 °C. Above 128 °C the authors observed an evolution of ammonia and the formation of undefined polymeric products.[12] Contrarily, Sprague et al. reported on the melting of $NH_4[N(CN)_2]$ around 140 °C. These authors postulated a reaction between NH_4^+ and $[N(CN)_2]^-$ ions leading to the formation of dicyandiamide (cyanoguanidine) $H_4C_2N_4$ (eq 1).[13] Furthermore, a thermally induced trimerization of the anions comparable to the situation of the alkali dicyanamides and formation of the tricyanomelaminate $(NH_4)_3[C_6N_9]$ might be possible.



1 **2** (eq. 1)

We synthesized ammonium dicyanamide $NH_4[N(CN)_2]$ through ion exchange in aqueous solution starting from $Na[N(CN)_2]$ and NH_4Cl.[15] According to the single-crystal

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* To whom correspondence should be addressed. E-mail: wolfgang.schnick@uni-muenchen.de.

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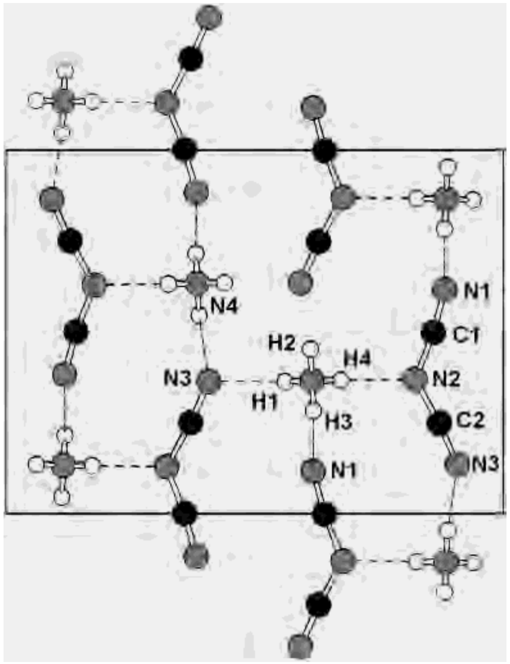

Figure 1. Crystal structure of $NH_4[N(CN)_2]$, view along [100] (C, black; N, gray; H, white).

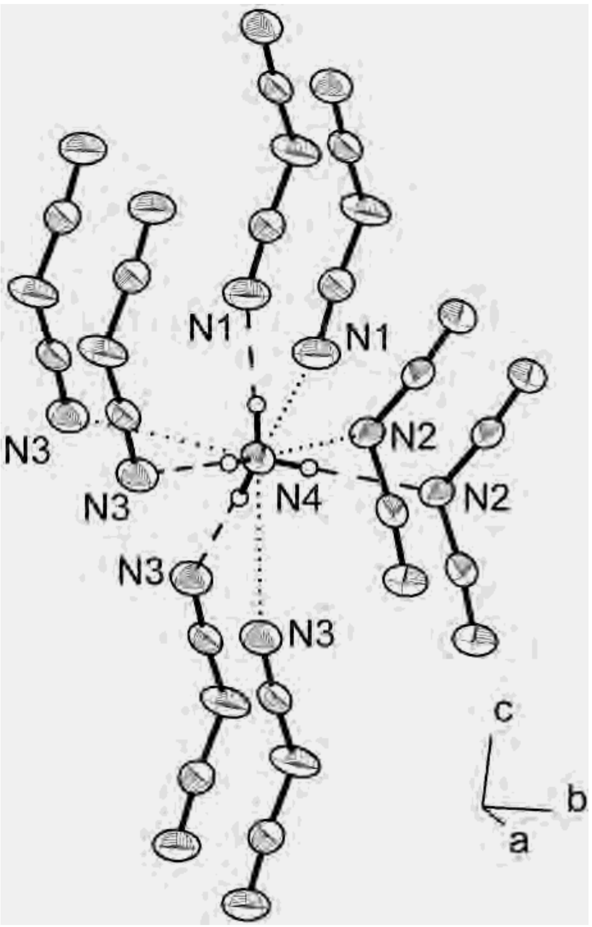

Figure 2. Coordination sphere of the NH_4^+ ion in $NH_4[N(CN)_2]$, with hydrogen bonds represented by broken lines; displacement ellipsoids are shown at the 70% probability level.

X-ray structure determination, $NH_4[N(CN)_2]$ is built up from tetrahedral NH_4^+ ions and bent planar $[N(CN)_2]^-$ ions (Figure 1).[16] The NH_4^+ ions are surrounded by the N atoms of eight $[N(CN)_2]^-$ ions forming a slightly distorted cube. Six terminal nitrogen atoms (2 × N1 and 4 × N3) as well as two bridging atoms N2 of the $[N(CN)_2]^-$ ions are involved in the coordination of the cation (Figure 2).

All of the hydrogen atoms have been localized during the structure determination. There are hydrogen bonds N4−H1···N3, N4−H2···N3, N4−H3···N1, and N4−H4···N2 (H···N, 198−219 pm; N4···N, 286−307 pm; N4−H···N, 169−177°); the distances agree well with those given in the literature for medium strong N−H···N hydrogen bonds.[18,19] The bond distances C−N to the bridging N atoms in the anions $[N(CN)_2]^-$ are significantly longer (131−132 pm) than those to the terminal N (115−116 pm), indicating single and triple bonds, respectively. The angles N−C−N are almost linear (173−174°), whereas the central angle C−N−C is 121°. These values are comparable to those of other dicyanamides.[5,11]

The crystal packing of cations and anions in $NH_4[N(CN)_2]$ resembles that of the CsCl structure type. None of the known dicyanamides with monovalent cations $M[N(CN)_2]$ (M = Na,[4] K,[5] Rb,[5] Cs,[20] Ag[21,22]) forms a similar structure. The crystal structure of α-$K[N(CN)_2]$ derives from that of KSCN by a simple replacement of N by NCN and S by N in the SCN^- ion.[5] Contrarily, there is no evidence for a similar relation between the crystal structures of NH_4OCN and $NH_4[N(CN)_2]$.

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(15) A column with an ion exchange resin (Merck, Ionenaustauscher I, Art. 4765) was completely filled with a solution of NH_4Cl (Fluka, ≥99.5% (AT)). An excess of NH_4Cl was removed by washing with water. Subsequently a solution of $Na[N(CN)_2]$ (Fluka, ≥96% (AT)) was poured onto the column. After evaporating of the water within some days at room temperature colorless needles of $NH_4[N(CN)_2]$ were formed.

(16) For the structure determination a single crystal (size 0.50 × 0.06 × 0.05 mm^3) was sealed inside a thin-walled glass capillary. X-ray diffraction data of 3620 reflections (953 independent, $R_{int} = 0.0604$) in the range $5.4° \leq 2\theta \leq 55.0°$ were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation (λ = 71.073 pm) at a temperature of $T = 200(2)$ K. The crystal structure of $NH_4[N(CN)_2]$ was solved by direct methods using SHELXTL[17] and refined with anisotropic displacement parameters for all atoms except the hydrogen atoms. Crystal data for $NH_4[N(CN)_2]$: $M = 84.09$ g mol^{-1}, $P2_1/c$ (No. 14), $a = 378.67(6)$ pm, $b = 1240.9(3)$ pm, $c = 911.84(14)$ pm, $\beta = 91.488(18)°$, $V = 428.32(13) \times 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.304$ g cm^{-3}, $\mu = 0.097$ mm^{-1}, 72 refined parameters, GOF = 0.816; R values for all data, R1 = 0.0775, wR2 = 0.0893.

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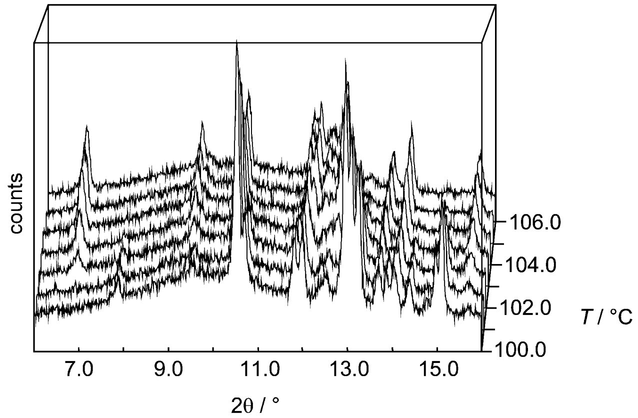

Figure 3. Temperature-dependent X-ray powder patterns of the phase transition of ammonium dicyanamide $NH_4[N(CN)_2]$ into dicyandiamide $H_4C_2N_4$ (Mo Kα_1 radiation, 100−106 °C in steps of 1 °C).

We performed thermoanalytical measurements and temperature-dependent X-ray powder diffraction experiments[23] to investigate the thermal behavior of ammonium dicyanamide. The DSC curve exhibits a sharp exothermic signal at 138 °C indicating an irreversible reaction with $\Delta H \approx -10$ kJ mol^{-1}. This corresponds with a solid−solid phase transition between 102 and 106 °C, which was identified by temperature-dependent X-ray powder diffraction (Figure 3). The temperature difference between both investigation methods is typical and presumably due to the much higher heating rate in the DSC experiment (5 °C min^{-1}). Neither the DSC experiment nor a visual inspection of the sample of $NH_4[N(CN)_2]$ during heating gave any evidence for a melting process of the substance in this temperature range. Furthermore, according to the X-ray diffraction the sample never was X-ray amorphous. After heating to 108 °C and subsequent cooling to room temperature the pattern indicated that $NH_4[N(CN)_2]$ quantitatively was transformed into dicyandiamide $H_4C_2N_4$. By further heating above 170 °C (Figure 4) the well-known transformation of dicyandiamide $H_4C_2N_4$ into melamine $H_6C_3N_6$ was observed.[24]

The powder diffraction patterns of the heated samples are in good agreement (Figure 4) with those simulated from structural data of dicyandiamide and melamine, respectively.[25,26]

The isomerization of $NH_4[N(CN)_2]$ into dicyandiamide $H_4C_2N_4$ represents an analogue to Wöhler's classical synthesis of urea by heating NH_4OCN:[27−30] The formal substitution of the O atom in NH_4OCN by the isolobal[31,32] cyanamide (carbodiimide) group N═C═N leads to ammonium dicyanamide $NH_4[N(CN)_2]$. Both salts NH_4XCN (X = O, NCN) undergo irreversible solid−solid transformations forming urea H_4CN_2O or dicyandiamide $H_4CN_2(NCN)$, respectively. In both cases no direct topological relation between the crystal structures of the ammonium salt NH_4XCN and the respective isomerization product H_4CN_2X was found.

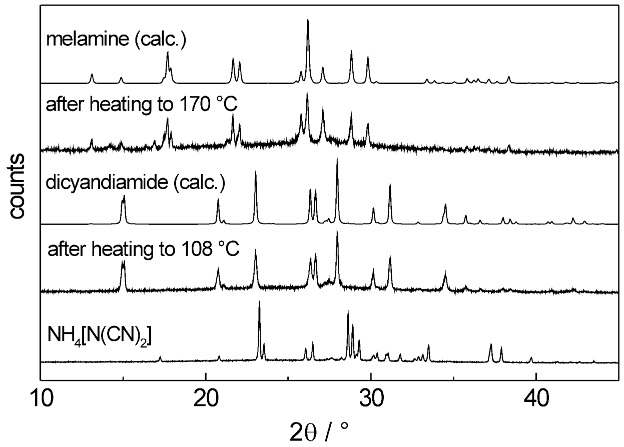

Figure 4. X-ray powder diffraction patterns (Cu Kα_1 radiation, measured at room temperature) of $NH_4[N(CN)_2]$ and its products after heating compared to diffraction patterns calculated from single-crystal diffraction data.

Further investigations are in progress to get a detailed picture of the mechanism of these solid-state transformations.[33]

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Supporting Information Available: Listings of the positional and thermal parameters, bond lengths and bond angles of $NH_4[N(CN)_2]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) A differential scanning calorimetry (DSC) curve of $NH_4[N(CN)_2]$ was recorded with a Mettler DSC 25 from 20 to 500 °C (heating rate: 5 °C min^{-1}).The temperature-dependent measurements between 100 and 120 °C were performed at atmospheric pressure on a STOE Stadi P powder diffractometer (Mo Kα_1 radiation) in Debye−Scherrer geometry with a computer-controlled furnace in steps of 1 °C.

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