Catalytic Formation and Crystal Structure of Cyanoguanylurea $H_2NC(=O)NHC(NH_2)NCN$

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The ion exchange reaction between ammonium cyanoureate $NH_4[H_2NC(=O)NCN]$ and zinc chloride yielded single crystals of the urea derivative cyanoguanylurea $H_2NC(=O)NHC(NH_2)NCN$, which was obtained as a by-product alongside zinc cyanoureate and traces of ammonium chloride. It is assumed that owing to its Lewis and Brønsted acidity, the hydrated Zn^{2+} ion acts as a catalyst, promoting the degradation of the cyanoureate anion with subsequent formation of the title compound. The crystal structure was solved in the centrosymmetric space group $P2_1/n$ ($a = 476.7(1)$, $b = 965.3(2)$, $c = 1165.6(2)$ pm, $\beta = 97.75(3)°$, $V = 531.4(2)\ 10^6$ pm^3, $Z = 4$, $T = 200$ K). In the solid there are non-planar cyanoguanylurea molecules with a dicyandiamide-type C-N system, building up a layered structure with sparse interlayer contacts and significant hydrogen bonding within the layers.

Key words: Zinc Catalysis, Crystal Structure, Cyanourea

Introduction

The importance of thermal condensation reactions for the synthesis of highly condensed phases or novel networked materials has stimulated detailed investigations of the reaction mechanisms of thermal solid-state reactions [1 – 5]. On this background, the thermal reactivity of simple inorganic nitridocarbonates(IV) such as cyanamides, dicyanamides, or tricyanomelaminates, which are discussed as potential molecular precursors for the prototype binary carbon nitride C_3N_4, was found to be particularly versatile. In a search for related systems with potentially similar solid-state reactivity, we synthesised the ammonium salt of *N*-cyanocarbamimidic acid [cyanourea (**1**)] (**2**), which can formally be derived from the C-N precursor ammonium dicyanamide (**3**) by addition of H_2O to one of the nitrile-groups (Scheme 1). The thermal reactivity of ammonium cyanoureate was studied in detail and classified as a complex thermal decomposition reaction proceeding in the solid-state [6]. The reaction pathway was retraced exclusively on the basis of spectroscopic evidence of the product distribution, leading to a qualitative picture of the mechanism on a molecular basis. Under optimised thermal conditions, cyanoguanyl-
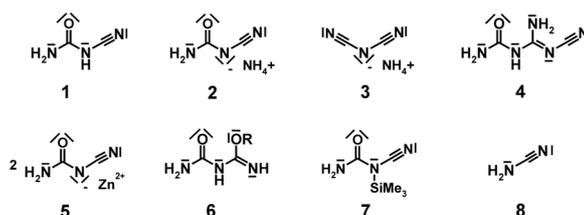
Scheme 1. Molecular formulas of cyanourea and structurally related species referred to in the text: (**1**) cyanourea, (**2**) ammonium cyanoureate, (**3**) ammonium dicyanamide, (**4**) cyanoguanylurea, (**5**) zinc cyanoureate, (**6**) carbamoyl-*O*-alkylisourea, (**7**) *N*-cyano-*N*-(trimethylsilyl)-urea, (**8**) cyanamide.

urea ([(cyanoamino)iminomethyl]-urea) (**4**) was observed as the main product along with varying amounts of urea. Owing to the difficulties in obtaining single crystals of the major decomposition product, ultimate evidence for the postulated structure, apart from NMR and other spectroscopic data, could not be given as yet.

In this contribution we present a novel synthetic approach to and the crystal structure of cyanoguanylurea and confirm the validity of our previously presented line of argument.

Table 1. Crystal data and structure refinement of [$H_2NC(=O)NHC(NH_2)NCN$].

Empirical formula	$C_3H_5N_5O$
Molar mass [$g\,mol^{-1}$]	127.12
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
T [K]	200
Z	4
a [pm]	476.7(1)
b [pm]	965.3(2)
c [pm]	1165.6(2)
β [°]	97.75(3)
V [$10^6\,pm^3$]	531.4(2)
Calculated density [$g\,cm^{-3}$]	1.589
Crystal size [mm^3]	$0.24 \times 0.13 \times 0.07$
Absorption coefficient [mm^{-1}]	0.127
$F(000)$	264
Diffraction range [°]	$3.53 \le \theta \le 27.50$
Index range	$-6 \le h \le 6,$
	$-12 \le k \le 11,$
	$-15 \le l \le 15$
Total no. reflections	9162
Independent reflections	1215
Observed reflections	1048
$R_{int}, F_o^2 \ge 2\sigma F_o^2$	0.0423
Refined parameters	103
Corrections	Lorentz,
	polarisation,
	extinction
GOF on F^2	1.081
Final R indices $|I > 2\sigma(I)|$	$R1 = 0.0357$
	$wR2 = 0.0964$
R Indices (all data)	$R1 = 0.0429$
	$wR2 = 0.1016$
	with $w = [\sigma^2(F_o^2)$
	$+(0.0510P)^2 + 0.1677P]^{-1}$
	where $P = (F_o^2 + 2F_c^2)/3$
Min./max. residual electron density [$e \cdot 10^{-6} \cdot pm^{-3}$]	$-0.219/0.193$

Table 2. Bond lengths [pm] and angles [°] for [$H_2NC(=O)NHC(NH_2)NCN$].

Distances		*Angles*	
O1-C1	123.5(2)	C2-N2-C1	126.3(2)
N1-C1	133.2(2)	C3-N3-C2	119.1(2)
N2-C2	136.7(2)	O1-C1-N1	123.8(2)
N2-C1	139.3(2)	O1-C1-N2	121.6(2)
N3-C3	132.0(2)	N1-C1-N2	114.6(2)
N3-C2	133.3(2)	N5-C2-N3	125.6(2)
N4-C3	116.4(2)	N5-C2-N3	120.7(2)
N5-C2	131.5(2)	N3-C2-N2	113.7(2)
		N4-C3-N3	173.2(2)
N1-H11	88(2)	C1-N1-H11	118(2)
N1-H12	88(2)	C1-N1-H12	120(2)
N2-H21	83(2)	H11-N1-H12	119(2)
N5-H51	95(2)	C2-N2-H21	115(2)
N5-H52	88(2)	C1-N2-H21	119(2)
		C2-N5-H51	118(1)
		C2-N5-H52	120(2)
		H51-N5-H52	122(2)
Hydrogen bonding:			
N1-H11···N4	214(2)	N1-H11-N4	179(2)
N1-H12···O1	226(2)	N1-H12-O1	146(2)
N2-H21···N3	215(2)	N2-H21-N3	168(2)
N5-H51···O1	198(2)	N5-H51-O1	130(2)
N5-H51···N4	237(2)	N5-H51-N4	134(2)
N5-H52···O1	206(2)	N5-H52-O1	162(2)

Experimental Section

Synthesis

Cyanoguanylurea (**4**) was obtained as a by-product in the synthesis of the zinc salt of cyanourea (**5**) from ammonium cyanoureate by ion metathesis in aqueous solution. Ammonium cyanoureate was synthesised from the free acid cyanourea and aqueous ammonia according to a procedure described elsewhere [6]. A column filled with 3 ml of a strongly acidic ion exchange resin (Ionenaustauscher I, H^+-Form, Art. 4765, Fa. Merck) was loaded with 20 ml of an aqueous solution containing 4.2 g of $ZnCl_2 (\ge 98\%,$ Fa. Merck). After washing with 200 ml of water, 12 ml of an aqueous solution of 0.2 g ammonium cyanoureate was poured onto the column. The eluate was evaporated at room temperature. Besides the polycrystalline main product, the title compound was obtained as a minor phase along with traces of ammonium chloride.

X-Ray-diffraction

X-ray diffraction data of a single crystal of **4** were recorded at 200 K on an ENRAF-NONIUS Kappa CCD four-circle diffractometer equipped with a rotating anode producing graphite monochromated Mo-K_α radiation ($\lambda = 71.073$ pm). The crystal structure was solved by direct methods using the program SHELXTS-97 [7] and refined on F^2 by the full-matrix least-squares method implemented in SHELXTL-97 [8]. No absorption correction was necessary due to the weak absorption coefficients of the constituent atoms. The positions of all hydrogen atoms could be determined unequivocally from difference Fourier syntheses, and all non-hydrogen atoms were refined anisotropically. Details of the structure determination and crystallographic data are summarised in Table 1. Intramolecular distances and angles are given in Table 2. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-414651, the name of the authors, and citation of the paper.

Vibrational spectroscopy

FTIR spectra were recorded on a Bruker IFS 66v/S spectrometer in the range from 400 to 4000 cm^{-1}. The samples were prepared as KBr pellets (5 mg sample, 500 mg KBr) under atmospheric conditions.

Results and Discussion

Formation

Previous synthetic approaches towards cyanoguanylurea in organic solvents utilised reactions between the urea derivative carbamoyl-*O*-alkylisourea (**6**) [9, 10] or trimethylsilylated cyanourea (**7**) with cyanamide (**8**) or cyanourea (**1**) [11], respectively. A simpler synthesis was proposed by Iio *et al.*, who obtained cyanoguanylurea from solutions containing free acid cyanourea or combinations of the latter with one of its salts [12] (Scheme 1).

Recently, we found that cyanoguanylurea was formed as a main product upon thermal decomposition of ammonium cyanoureate alongside varying amounts of urea. We assume the thermal reaction to be dominated by the role of the ammonium ion, in that the latter acts both as proton transfer agent and as a nucleophile leading to the cleavage of the C(=O)-NCN single bond of ammonium cyanoureate (**2**) [6].

In the present case, ammonium cyanoureate was added to an ion exchange resin, whose acidic sites had been loaded with an aqueous ZnCl$_2$ solution. It is well-known that despite thorough washing small amounts of a salt solution may be adsorbed by the resin, depending on the ionic interactions with the matrix, and subsequently released upon consecutive exchange steps.

The latter scenario may be applicable also in this case, as evidenced by the presence of traces of NH$_4$Cl in the product mixture alongside cyanoguanylurea (**4**) and the main product zinc cyanoureate (**5**). This is indicative of an incomplete removal of ZnCl$_2$ after the loading and washing procedures. A potential formation mechanism of **4** may therefore be proposed as follows:

ZnCl$_2$ is assumed to stimulate the molecular degradation pathway, which otherwise is induced thermally in a like manner [6]. The cleavage of the C(=O)-NCN single bond, which can thermally be stimulated by a proton transfer from the ammonium ion to the oxygen atom, can be effected by ZnCl$_2$ in two ways: By coordination of ZnCl$_2$ to the oxygen atom, the C(=O)-NCN single bond becomes strongly polarized, leading to subsequent cleavage with formation of hydrogen isocyanate, cyanamide and ammonia or related species after proton transfer reactions. A more simple explanation is invoking the Brønsted acidity of concentrated aqueous solutions containing Zn^{2+} species:

As was reported previously, cyanoguanylurea is formed in a slow reaction in aqueous and organic solu-

tions containing the free acid cyanourea together with a cyanoureate salt [6, 12]. In an investigation of the influence of pure Brønsted acidity on the formation of cyanoguanylurea, the attempt of a quantitative synthesis of cyanoguanylurea from ammonium cyanoureate in mildly (pH $\approx$ 3, HCl) acidic aqueous solution led to the formation of cyanourea and ammonium chloride only. In strongly acidic solution (pH $\approx$ 1, HCl), cyanourea and ammonium chloride were formed together with an unknown phase.

Consequently, the title compound will only be formed in the presence of Brønsted acids *via* the intermediate formation of cyanourea and subsequent reaction of the latter with unreacted ammonium cyanoureate, but not if cyanourea is formed quantitatively. Therefore, we assume that in the present case cyanoguanylurea is obtained by the interplay between the Brønsted and Lewis acidic character of aqueous Zn^{2+} solutions, the latter of which plays the decisive role in the decomposition reaction.

Given that the formation of cyanoguanylurea only occurs as a minor side reaction, the exact stoichiometry of the overall reaction cannot be resolved. Furthermore, for the same reason the outline of the tentative reaction mechanism appears to be critical, since the nature of the species actually involved cannot be verified. However, in light of the corresponding product formation by either thermal treatment or the presence of ZnCl$_2$ in an ammonium cyanoureate solution, the acid ZnCl$_2$ may be assumed to act as a catalyst in the fragmentation of the cyanoureate anion. In a subsequent step, addition of cyanamide to another cyanoureate anion may occur, resulting in the formation of cyanoguanylurea (Scheme 2).
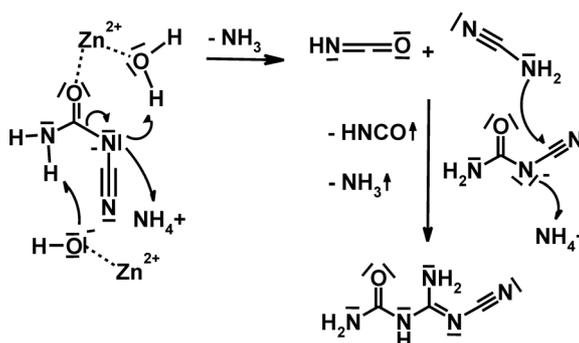
Scheme 2. Tentative mechanism for the formation of cyanoguanylurea from ammonium cyanoureate in the presence of ZnCl$_2$. The Zn^{2+} species in aqueous solution are only drawn schematically so as to indicate their function.
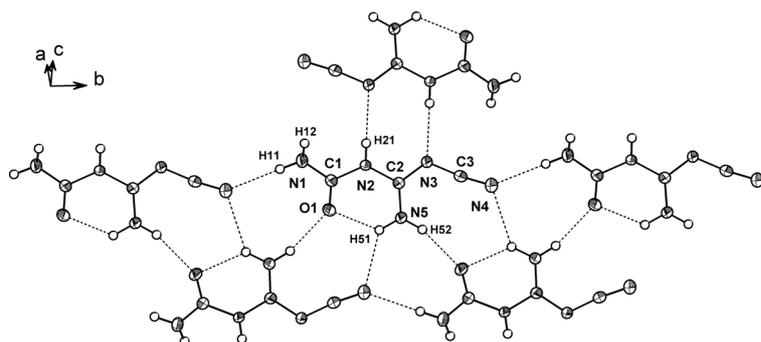
Fig. 1. Environment of the cyanoguanyl-urea molecule in a layer formed by a hydrogen bonding network (dotted lines). The displacement ellipsoids are drawn at the 50% probability level.

Another question to be addressed is the poor water solubility of cyanoguanylurea, and hence, the inhibited crystallization from aqueous solution observed in the previous investigations [6]. The fact that the opposite was found in the present study, namely the facile crystallization from aqueous solution, suggests a significant increase in water solubility, presumably owing to the different pH of the solution due to the slightly acidic character of ZnCl$_2$. The tendency towards crystallization may, however, also result from the presence of NH$_4$Cl which has been reported in the literature to act as a mineralizer [13–17].

Crystal structure

Cyanoguanylurea crystallizes in the monoclinic crystal system, space group $P2_1/n$ (no. 14), with four formula units in the unit cell. As proposed in our previous study on the thermally induced formation of the title compound [6], the molecule has a cyanoguanylurea structure (Fig. 1) and not that of its isomer cyanocarbamoylguanidine.

All protons could be unambiguously localized at N1, N2 and N5. Thus, the 'imino' tautomer (H$_2$N)(HRN)C=NCN (R = H, organic residue) rather than the 'amino' tautomer (HRN)(HN=)CNHCN represents the molecular structure of cyanoguanylurea as also found for dicyandiamide (cyanoguanidine) as well as of some *N*-cyano-*N'*-substituted guanidines both in solution and in the solid state [18–25]. By analogy with the structural data reported for the prototype structure of dicyandiamide [18,19], the bonding situation is not fully accounted for by assuming the prevalence of the resonance structure **a** as depicted in Scheme 3. Although drawing a double bond between C2 and N3 appears to be energetically reasonable in terms of conjugation and mandatory in view of the experimentally found proton distribution, the adja-

cent bond distances C3-N3 [132.0(2) pm] and C2-N5 [131.5(2) pm], though formally drawn as single bonds (Scheme 3**a**), are shorter than C2-N3 [133.3(2) pm], their values all being intermediate between those of a single and a double bond. This finding is indicative of π electron density equally distributed over parts of the guanidine system (N5-C2-N3) as well as the N3-C3 bond. This suggests that structures **b–e** jointly contribute as much as **a** to the total valence structure. This phenomenon is frequently encountered in structures containing the cyanoguanidine unit [18–25], indicating the conventionally reported structure for cyanoguanidine derivatives to be rather simplistic and inappropriate if the contributing charge separated forms **b–e** are neglected [18–20]. Although the C3-N4 distance of 116 pm is indicative of the cyanamide and not the carbodiimide structure to represent the bonding situation most appropriately, the N3-C3-N4 moiety is slightly bent ($\angle 173.3°$) and the atomic displacement ellipsoid of C3 is not elongated
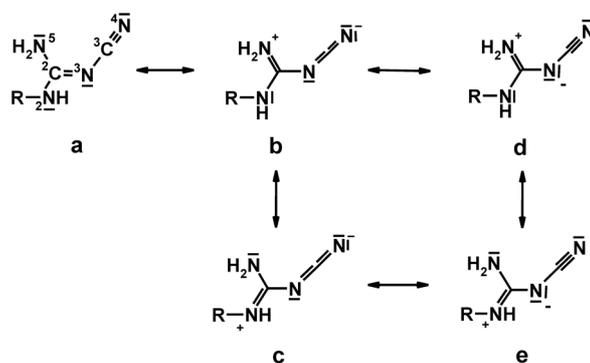
Scheme 3. Resonance structures of *N*-cyano-*N'*-substituted guanidines. The 'true' electronic structure may be considered as a superposition of the neutral structure **a** and the charge separated structures **b** and **d**. Given the relatively long bond length C2-N2, structures **c** and **e** obviously contribute to a lesser extent in cyanoguanylurea.
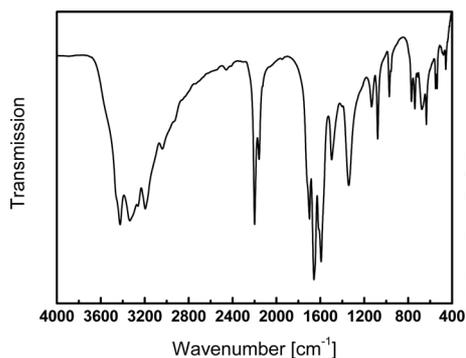
Fig. 2. FTIR spectrum of cyanoguanylurea, recorded at room temperature.
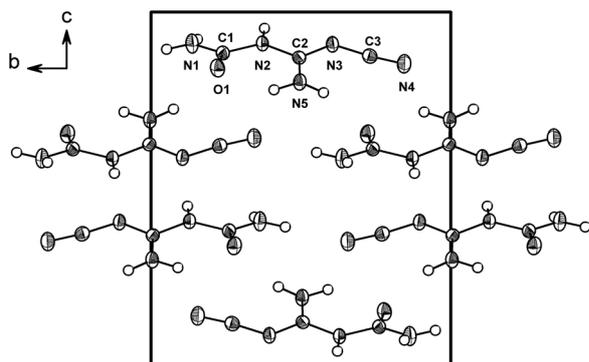
Fig. 3. Unit cell of cyanoguanylurea, view along [100]. The displacement ellipsoids are drawn at the 50% probability level.

perpendicular to the molecular plane as is observed for the adjacent atoms N3 and N4. This finding may not be an artifact but truly reflect the 'superposition' of structures **a**, **d** and **e** on the one hand, and **b** and **c** with two adjacent allenic double bonds on the other hand, thus dislocating the electron density of C3 *along* and not *perpendicular* to the N3-C3-N4 bond system.

The nitrile region in the IR spectrum of cyanoguanylurea showing a doublet at 2199 (s) / 2158 cm^{-1} (w) is very similar to that of dicyandiamide [2202 (s) / 2160 cm^{-1} (w)] which may also serve as evidence for a similar electron density distribution in the two related compounds (Fig. 2).

The molecule is embedded in a hydrogen bonding network, comprising medium strong and weak hydrogen bonds (H$\cdots$N/O $\approx$ 210–240 pm). The intramolecular contact N5-H51$\cdots$O1 represents the strongest hydrogen bond, resulting in a six-membered "chelate ring" reminiscent of keto-enol tautomeric systems.
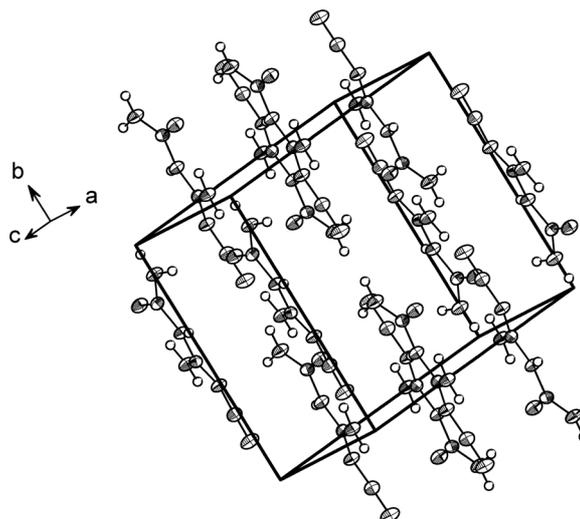
Fig. 4. Layered structure of cyanoguanylurea made up from hydrogen-bonded molecules: View along the planes spanned by [010] and [301]. The displacement ellipsoids are drawn at the 50% probability level.

This interaction seems to direct the structural arrangement, which significantly deviates from molecular planarity: Whereas the cyanoguanidine fragment is almost planar (torsion angle C2-N2-N3-C3 = 179°), the urea unit is twisted with respect to the former around the C1-N2 bond, thus introducing torsion angles N1-C2-N2-C3 of 164° and O1-C2-N2-C3 of 16°, thereby circumventing an eclipsed arrangement of the atoms (Fig. 3). This situation may explain the virtual absence of π-delocalization into the C2-N2 bond of the guanidine system [136.7(2) pm], since potential conjugation with the C1-O1 double bond is reduced by the above twisting.

The molecules are stacked along the b-axis, forming planes extending in the [301] direction (Fig. 4). While the planes are spaced by about 470 pm, the shortest "interplanar" distances are the hydrogen bonding contacts between O1 and H12 which are as short as 230 pm. However, owing to the relatively sparse interactions between the planes, the crystal structure of cyanoguanylurea may be considered as a layered structure, the layers being made up from hydrogen bonded molecular units.

Conclusion

Cyanoguanylurea has been obtained from aqueous solutions containing traces of the Lewis acid $ZnCl_2$

and ammonium chloride, where the function of the former seems to be that of a catalyst, while the latter may act as a mineralizing agent. The crystal structure of cyanoguanylurea is composed of molecular units, whose molecular structure is fully consistent with that previously proposed for the title compound on the basis of IR and NMR spectroscopic data. Cyanoguanylurea represents yet another cyanoguanidine derivative, the electronic structure of which can only be described adequately by invoking the contribution of several charge separated structures in addition to the neutral prototype structure with a conjugated π-system.

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