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Neutron powder diffraction and theory-aided structure refinement of rubidium and cesium ureate

Abstract: Urea (CN_2H_4O) is a fundamental biomolecule whose derivatives are abundant throughout chemistry. Among the latter, rubidium ureate ($RbCN_2H_3O$) and its cesium analog ($CsCN_2H_3O$) have been described only very recently and form the first structurally characterized salts of deprotonated urea. Here, we report on a neutron diffraction study on the aforementioned alkaline-metal ureates, which affords the positions for all hydrogen atoms (including full anisotropic displacement tensors) and thus allows us to gain fundamental insights into the hydrogen-bonding networks in the title compounds. The structure refinements of the experimental neutron data proceeded successfully using starting parameters from *ab initio* simulations of atomic positions and anisotropic displacement parameters. Such joint experimental-theoretical refinement procedures promise significant practical potential in cases where complex solids (organic, organometallic, framework materials) are studied by powder diffraction.

Keywords: anisotropic displacement parameters (ADPs); density-functional theory (DFT); hydrogen bonding; neutron crystallography; urea.

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1 Introduction

Urea (CN_2H_4O) is a fundamental biomolecule and is utilized in pharmaceuticals, cosmetics, colorants, or fertilizers [1]. Likewise, urea has been a topic of fundamental studies for long: it crystallizes in the tetragonal space group $P\overline{4}2_1m$ with full ($mm2$) point symmetry resulting in a minimum of atomic parameters to be refined [2]. The carbonyl oxygen atom of the urea molecule takes part in the crystal in four N–H⋯O hydrogen bonds (HBs) [2, 3] which has placed urea among the most widely studied prototype systems for HB interactions in solids [4]. In general, HBs are of paramount interest because of their presence in biochemical compounds such as nucleic acids of living cells and amino acids. In proteins, HBs influence structure, specificity, and functionality through their role in the folding process [5]. Furthermore, these HBs play a pivotal role by enabling *N,N*′-disubstituted ureas to build chains, layers, three-dimensional frameworks, or even nanotubes [6]. Besides, when suppressing these HBs between the ureas through introduction of certain substituents, the ureas can form HBs with neutral species or anions, preferably oxoanions, providing metal-organic frameworks with anion separation selectivities [6]. Further Ni, Zr and Fe complexes with *N,N*′-disubstituted ureate ligands have been reported [7–13], finding use, e.g. in organometallic catalysis [7–9].

In principle, the free urea molecule should also be amenable to deprotonation, and indeed as early as in 1902 Franklin [14] (most likely) removed a proton from urea and, by doing so, synthesized KCN_2H_3O. This work was followed three decades later by Jacobson [15] who reported $NaCN_2H_3O$ in 1936, but such compounds were not fully characterized. Only very recently, the class of deprotonated urea salts ("ureates") was extended by $RbCN_2H_3O$ and $CsCN_2H_3O$ [16], and at the same time, the first structural characterization of the above-mentioned compounds $NaCN_2H_3O$ and KCN_2H_3O was achieved using single-crystal X-ray diffraction (SC-XRD) [16].

Here, we report on neutron diffraction experiments that complete the structural characterization of rubidium and cesium ureate. This enables a closer study of their HB networks, also in comparison to the parent compound urea, which is of interest with regard to their importance in *N,N′*-disubstituted urea(te) compounds (Fig. 1). It is also worthwhile pointing out the parallels to the recently reported family of alkali-metal guanidinates [17–20], which are likewise paralleled by a large range of substituted guanidinates in organic chemistry.

At the same time, the title compounds are ideally suited to address a prevalent practical problem that occurs even if neutron diffraction measurements can be carried out: incoherent scattering may lead to a significantly higher background whose treatment is far from trivial, and the determination of ADPs becomes particularly challenging when reflections with low *d*-values have low intensity and overlap extensively. Furthermore, mutually influential parameters may complicate the refinement. In such cases, a suitable choice of starting values for the parameters is crucial.

To alleviate this problem, we here follow a hybrid approach in which the experimental data is complemented by *ab initio* quantum-chemical computations – an overall strategy that has turned out highly fruitful in the past, e.g. for hybrid experimental-theoretical structure solutions from scratch [21], or for the accurate positioning of hydrogen atoms in routine X-ray crystallographic studies [22]. To arrive at a stable refinement over the entire range of signals, we here chose to calculate starting values for the atom positions with DFT, but furthermore to also derive ADPs from DFT-based phonon computations, all as suggested recently [23]. In the past, such analyses have been done for several different molecular crystals with highly encouraging results (see Ref. [23] and references therein), but until now they have been done *a posteriori* – based on finalized (and successful) refinements, holding the calculated ADPs up against the experimental benchmark. By contrast, we here argue that the use of periodic DFT starting values for both atomic positions *and* phonon-derived ADPs holds great promise in speeding up refinement procedures – or in making them possible at all.

2 Results and discussion

2.1 From neutron experiments to a hybrid refinement

The Rietveld refinement plots resulting from the neutron experiments on $RbCN_2H_3O$ and $CsCN_2H_3O$ are shown in Figs. 2 and 3, and important parameters from these refinements are listed in Tables 1 and 2. All diffractograms exhibit rather high background due to incoherent scattering from hydrogen atoms – the very problem discussed in the Introduction. Additionally, absorption and preferred orientation of the crystals in the powder samples has to be taken into account.

An overview of the lattice parameters of $RbCN_2H_3O$ and $CsCN_2H_3O$ is given in Table 3, comparing results

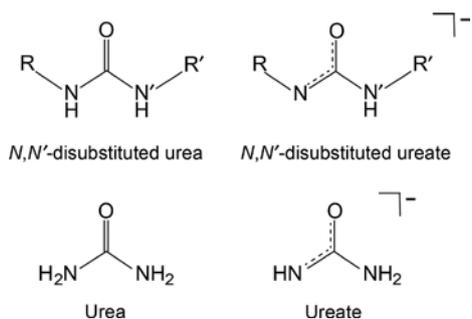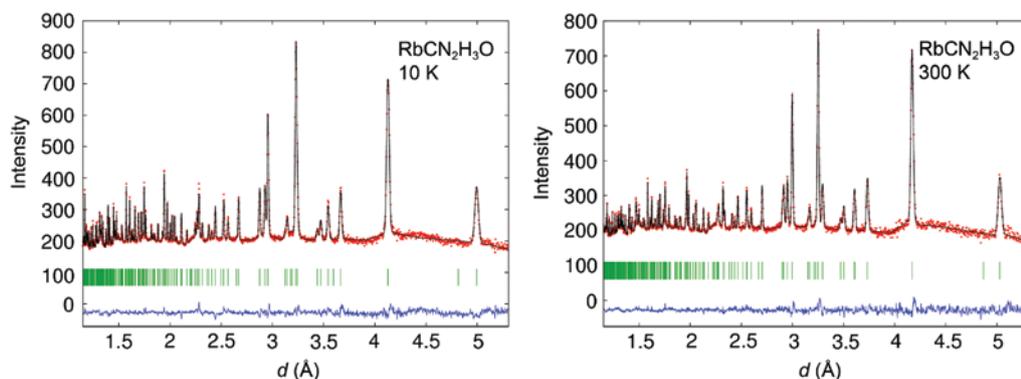**Fig. 1:** Structure of *N,N′*-disubstituted urea, urea and the ureate anions.

Fig. 2: Rietveld refinement plot of $RbCN_2H_3O$ at *T* = 10 K and 300 K for wavelength band λ_{center} = 1.333 Å.

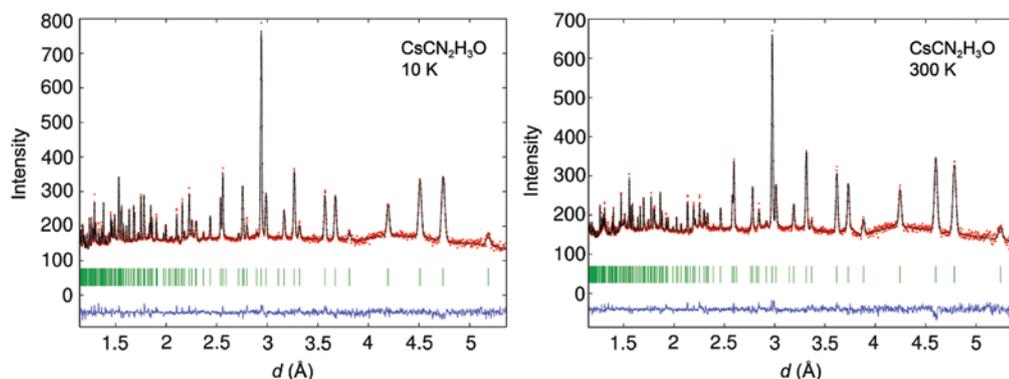**Fig. 3:** Same as in Fig. 2 but for CsCN₂H₃O.

Table 1: Parameters attained from the simultaneous Rietveld refinement of the neutron powder diffraction data of RbCN$_2$H$_3$O for wavelength bands with λ_{center} = 1.333 Å and λ_{center} = 2.665 Å.

T, K	10	300
Space group	*Pbca* (no. 61)	
a, Å	7.1918(8)	7.2252(7)
b, Å	7.3329(5)	7.4669(5)
c, Å	13.8874(1)	14.0105(3)
V, Å³	732.37(14)	755.86(14)
Refined pattern range,	26 000–120 000/	26 000–120 000/
t.o.f. (μs)	26 000–140 000	26 000–140 000
Absorption parameter	0.015(2)/0.016(1)	0.012(3)/0.011(2)
R_p	0.0201/0.0192	0.0189/0.0126
R_{Bragg}	0.0740/0.0711	0.0547/0.0633

Table 2: Parameters attained from the Rietveld refinement of the neutron powder diffraction data of CsCN$_2$H$_3$O for the wavelength band with λ_{center} = 1.333 Å.

T, K	10	300
Space group	$P2_12_12_1$ (no. 19)	
a, Å	6.3358(2)	6.3779(1)
b, Å	7.1393(2)	7.2349(9)
c, Å	9.0193(8)	9.1996(2)
V, Å³	407.97(6)	424.50(7)
Refined pattern range, t.o.f. (μs)	26 000–121 600	26 000–121 600
Absorption parameter	0.046(2)	0.031(2)
R_p	0.0232	0.0209
R_{Bragg}	0.104	0.0822

obtained with different diffraction methods and also at various temperatures. The results of the present neutron diffraction data refinement are favorably in line with those of previous experiments using different techniques and temperatures.

To attain sensible values for all refinable parameters one is crucially dependent on well-chosen starting values. This was easily confirmed for the title compounds: using ADPs that had been routinely converted from the SC-XRD isotropic displacement parameters led to unphysical, partly negative ADPs for the hydrogen atoms. Furthermore, the refinement of the hydrogen positions proved to be rather time-consuming. This is caused by the large number of interdependent parameters, which may lead to good refinements but chemically incorrect values for some parameters, especially when the starting values are not carefully (enough) chosen. By contrast, using starting values from DFT-based phonon calculation and applying soft restraints gave a good refinement with positive ADPs and atomic distances showing a good correlation with those from urea and the guanidinate analog RbCN$_3$H$_4$.

2.2 Displacement ellipsoids

Figure 4 shows the calculated and the refined displacement ellipsoids for the molecular anion in RbCN$_2$H$_3$O and CsCN$_2$H$_3$O at T = 10 K. The overall agreement manifests that such a calculation affords reasonable starting values for the (hydrogen) positions and ADPs, which makes the refinement more efficient – or even possible in the first place, as witnessed here.

A full list of the equivalent displacement parameters U_{eq} for RbCN$_2$H$_3$O and CsCN$_2$H$_3$O at both T = 10 and 300 K, and for urea at T = 12 K [2] and 293 K [3] is given in Table 4. As expected, the U_{eq} of RbCN$_2$H$_3$O and CsCN$_2$H$_3$O closely resemble those encountered in pure urea at lowest temperature, where the atomic motion is small. At T = 300 K the values for U_{eq} of RbCN$_2$H$_3$O and CsCN$_2$H$_3$O are quite similar among themselves, but clearly smaller than those of urea at T = 293 K. The same is observed when comparing the archetypical guanidinate, RbCN$_3$H$_4$, to the neutral parent compound guanidine [19, 24]. It seems that the electrostatic forces between the molecular anions and

Table 3: Lattice parameters of $RbCN_2H_3O$ and $CsCN_2H_3O$ from different diffraction methods and at different temperatures.

	Method	T (K)	a (Å)	b (Å)	c (Å)	V (Å³)
$RbCN_2H_3O$	P-ND	10	7.1918(8)	7.3329(5)	13.8874(1)	732.37(14)
	SC-XRD [1]	100	7.1973(8)	7.3531(8)	13.9214(15)	736.75(14)
	P-XRD	295	7.218(5)	7.464(5)	14.001(8)	754.3(15)
	P-ND	300	7.2252(7)	7.4669(5)	14.0105(3)	755.86(14)
$CsCN_2H_3O$	P-ND	10	6.3358(2)	7.1393(2)	9.0193(8)	407.97(6)
	SC-XRD [1]	100	6.3520(3)	7.1645(4)	9.0911(5)	413.73(4)
	P-XRD	295	6.370(4)	7.227(8)	9.188(7)	423.0(11)
	P-ND	300	6.3779(1)	7.2349(9)	9.1996(2)	424.50(7)
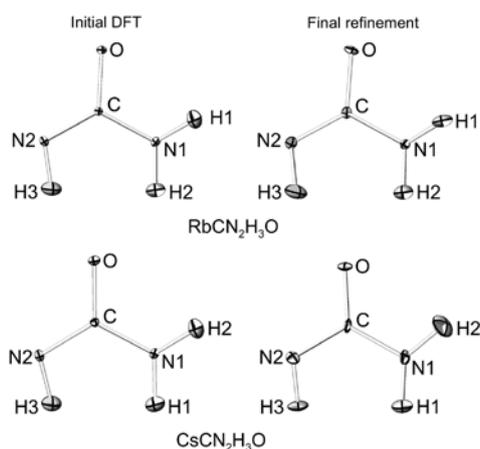
Fig. 4: $CN_2H_3O^-$ anion in $RbCN_2H_3O$ (top) and in $CsCN_2H_3O$ (bottom) with the initial DFT-computed (left) and the final refined (right) ellipsoids drawn at a probability of 50 % for the temperature of $T = 10$ K.

metal cations hinder the "free" molecular motion seen in urea, where only HBs are holding the molecules together.

Figures 5 and 6 show the displacement ellipsoids based on the neutron experiments for the ureate anion in $RbCN_2H_3O$ and $CsCN_2H_3O$, respectively. The hydrogen atoms exhibit a rather significant displacement at

$T = 10$ K, whereas the atoms in the central OCN_2 fragment are moving very little. At $T = 300$ K, the displacement parameters of atoms in the OCN_2 framework are enlarged to almost the fourfold, while those of the hydrogen atoms are less than doubled.

2.3 Molecular structures, hydrogen-bonding parameters, and their relation to free urea

With the nuclear positions of the hydrogen atoms attained from the neutron data it is now possible to determine all bond lengths and angles of the $CN_2H_3O^-$ anion in $RbCN_2H_3O$ and $CsCN_2H_3O$, as listed in Tables 5 and 6. The bond lengths and angles in the OCN_2 fragment are in good agreement with those determined by SC-XRD. The C–N2 bond, as expected, is slightly shorter than C–N1 both for $RbCN_2H_3O$ and $CsCN_2H_3O$. This is caused by the partial double-bond character between the atoms C and N2 [1], which also leads to a lengthening of the C=O bonds. Likewise, the C–N1 bonds are longer than the corresponding bonds in urea. We could not find any general difference in the N–H bond lengths between the imine and amine group. At $T = 10$ K, all N–H bonds lengths determined in

Table 4: Equivalent displacement parameters U_{eq} (Å²) in $RbCN_2H_3O$, $CsCN_2H_3O$ and in the free parent compound urea (CN_2H_4O), measured at $T = 10$ K (12 K) and 300 K (293 K), respectively.

	Low-temperature studies			Ambient-temperature studies		
	$RbCN_2H_3O$	$CsCN_2H_3O$	CN_2H_4O [2]	$RbCN_2H_3O$	$CsCN_2H_3O$	CN_2H_4O [3]
T, K	10	10	12	300	300	293
Rb/Cs	0.004(2)	0.006(7)	–	0.024(3)	0.037(9)	–
C	0.005(3)	0.007(7)	0.0054(4)	0.017(4)	0.022(8)	0.0287(6)
O	0.007(3)	0.009(7)	0.0069(5)	0.024(3)	0.029(8)	0.0391(8)
N1	0.006(2)	0.009(6)	0.00950(17)	0.026(3)	0.033(6)	0.0545(5)
N2	0.0060(19)	0.008(5)	–	0.022(2)	0.028(5)	–
H1	0.020(5)	0.020(14)	0.0246(9)	0.037(7)	0.036(16)	0.0718(18)
H2	0.019(5)	0.022(14)	0.0235(7)	0.039(7)	0.040(15)	0.0658(13)
H3	0.021(5)	0.020(13)	–	0.041(7)	0.042(18)	–
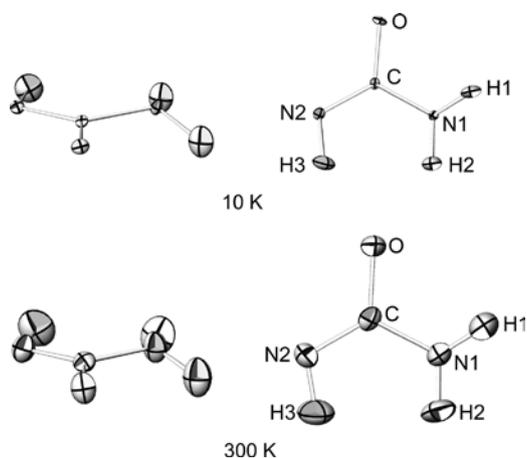
Fig. 5: $CN_2H_3O^-$ anion in $RbCN_2H_3O$ with refined displacement ellipsoids drawn at a probability of 50 % for the temperatures $T = 10$ K (top) and 300 K (bottom).
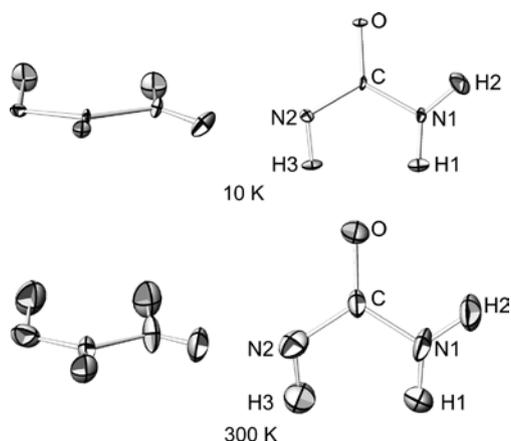
Fig. 6: Same as in Fig. 5 but for $CsCN_2H_3O$.

Table 5: Bond lengths (Å) and angles (deg) for the $CN_2H_3O^-$ anion in $RbCN_2H_3O$.

Method	P-ND	SC-XRD [1]	P-ND
T, K	10	100	300
O–C	1.303(4)	1.290(2)	1.293(5)
C–N1	1.383(2)	1.393(3)	1.390(2)
C–N2	1.316(3)	1.315(3)	1.308(4)
N1–H1	1.032(5)	0.85(3)	1.016(7)
N1–H2	1.011(4)	0.84(3)	1.013(5)
N2–H3	1.022(6)	0.82(3)	1.027(7)
O–C–N1	114.0(4)	115.34(18)	114.4(4)
N1–C–N2	123.2(3)	122.59(19)	122.9(3)
H1–N1–H2	114.3(7)	119(3)	116.7(10)
C–N2–H3	112.8(6)	109.9(19)	110.0(7)

neutron experiments arrive at $d(\text{N–H}) \approx 1.02(1)$ Å. These are well in line with those for urea at $T = 12$ K, $d(\text{N–H1}) = 1.008(4)$ Å and $d(\text{N–H2}) = 1.001(4)$ Å [2].

Table 6: Bond lengths (Å) and angles (deg) for the $CN_2H_3O^-$ anion in $CsCN_2H_3O$.

Method	P-ND	SC-XRD [1]	P-ND
T, K	10	100	300
O–C	1.284(8)	1.278(4)	1.272(11)
C–N1	1.377(6)	1.383(4)	1.383(7)
C–N2	1.339(6)	1.334(4)	1.340(7)
N1–H1	1.024(11)	0.92(4)	1.026(13)
N1–H2	1.028(11)	0.91(4)	1.030(13)
N2–H3	1.024(10)	0.95(5)	1.023(12)
O–C–N1	122.4(7)	116.8(4)	123.5(10)
N1–C–N2	119.7(5)	120.5(4)	114.9(6)
H1–N1–H2	132.4(19)	117(5)	126(2)
C–N2–H3	112.7(11)	108(3)	115.2(14)

Based on the SC-XRD experiments HB networks were proposed for urea-type systems by Sawinski [1], only knowing the positions of the donor atom D and the acceptor atom A, using the terminology for the HBs based on D(donor)–H(hydrogen)⋯A(acceptor) [25]. Based on the angle D–H⋯A and the D–H and H⋯A distances, more information is gained. With the hydrogen nuclei's positions and associated angles from the neutron diffraction experiments we are now able to study the HBs more accurately. The putative HB network in $RbCN_2H_3O$ has here been confirmed and that in $CsCN_2H_3O$ has been revised; for the latter, an additional hydrogen bond between H3 and O was found. Considering that the donor⋯acceptor distance for the HB N2⋯O is close to 3.2 Å where HBs have been argued to "fade out" [26], its existence could be discussed. With the additional information about the H3⋯O distance and the N2–H3⋯O angle, from our point of view it can now be considered an HB if one accepts the HB classification by Jeffrey [26]. Finally, these HBs could be compared to those in the parent compound urea. Structural parameters for all HBs in $RbCN_2H_3O$, $CsCN_2H_3O$, and also in urea are listed for $T = 10$ K (12 K) in Table 7, with quite similar values at $T = 300$ K (293 K). The bond lengths increase by a maximum of 5 % from $T = 10$ K to 300 K while the HB angles differ at most by 2 %.

Each hydrogen atom in urea forms an HB to an oxygen atom and, as a result, each oxygen atom accepts four HBs which, due to the two symmetry-inequivalent hydrogen atoms, have slightly different lengths [2, 3]. In $RbCN_2H_3O$, as in urea, HBs are formed between the oxygen atom and the amino hydrogen atoms (which are here labeled as H1 and H2). The imino hydrogen (H3) does not play any part in the HB network, in line with the all-nitrogen analog guanidine where the imino group does not form (relevant) HBs [27]; note that the imino atom is the key HB acceptor in guanidine (in the ureates, by contrast, oxygen atoms

Table 7: HB bond lengths (Å) and associated angles (deg) in $RbCN_2H_3O$, $CsCN_2H_3O$, and CN_2H_4O, at T = 10 K (12 K for free urea).

	$RbCN_2H_3O$		$CsCN_2H_3O$		CN_2H_4O [2]	
	d(H···A)	∠(D–H···A)	d(H···A)	∠(D–H···A)	d(H···A)	∠(D–H···A)
N(1)–H1···O	1.968(6)	174.6(5)			1.992(2)	167.2(2)
N(1)–H2···O	2.079(6)	152.1(4)			2.058(2)	147.4(2)
N2–H3···O			2.175(12)	171.2(9)		
N1–H1···N2			2.106(12)	155.6(9)		
N1–H2···N2			2.008(11)	171.2(8)		

are available as acceptors). $CsCN_2H_3O$, on the other hand, exhibits HBs between the oxygen atom and the hydrogen atom H3, while the other two hydrogen atoms H1 and H2 extend HBs to the nitrogen atom N2. The length of the HBs in $RbCN_2H_3O$ is a bit shorter for the H1···O and a bit longer for the H2···O compared to those in CN_2H_4O with their associated angles being closer to 180°. Based on bond lengths and angles all these HBs are classified as "moderate", again following the classification by Jeffrey [26].

A look at the donor-acceptor distances allows one to discern a clearer tendency. From urea via $RbCN_2H_3O$ to $CsCN_2H_3O$, there is an increase in the distances. In urea, the donor-acceptor distances are d(N(H1)···O) = 2.985(1) Å and d(N(H2)···O) = 2.955(1) Å [2], whereas in $RbCN_2H_3O$ the distances are d(N1(H1)···O) = 2.997(4) Å and d(N1(H2)···O) = 3.010(4) Å. In $CsCN_2H_3O$, the distances are larger, namely d(N1(H1)···N2) = 3.067(6) Å, d(N1(H2)···N2) = 3.028(5) Å and d(N2(H3)···O) = 3.190(8) Å. The increase in the donor-acceptor distances from urea to $RbCN_2H_3O$ and onwards to $CsCN_2H_3O$ is clearly due to the introduction of metal ions of different size [28].

The HB networks are shown in Fig. 7 for both $RbCN_2H_3O$ and $CsCN_2H_3O$. The HB network in $RbCN_2H_3O$

Fig. 7: HB networks in $RbCN_2H_3O$ (left) and $CsCN_2H_3O$ (right), with both views along [100]. The metal atoms are suppressed to emphasize the connectivity of the molecular anions. The oxygen atoms are colored in blue, carbon in black, nitrogen in green, and hydrogen in gray.

forms layers in direction of the c axis. Between the anion layers, a double layer of metal atoms is found. Each anion layer consists of a zigzag chain with $CN_2H_3O^-$ anions alternating with a rotation of 180° in direction of the b axis, and the chains are stacked along the a axis. $CsCN_2H_3O$, on the other hand, exhibits a three-dimensional HB network, forming tunnels in direction of the a axis in which metal atoms are located.

3 Conclusion

Two uncommon compounds of de-protonated free urea, namely, crystalline rubidium and cesium ureate, have been studied by neutron diffraction. Due to inherent limitations in neutron powder diffraction, starting parameters for the structure refinement were obtained from *ab initio* simulations of atomic positions and ADPs; with this theoretical aide at hand, the subsequent refinement of experimental data proceeded successfully. This hybrid refinement approach could prove useful in the future for the (ubiquitous) cases where low sample crystallinity, high absorption and/or peak overlap pose challenges to the experimentalist.

At low temperature, urea and both of its salts $RbCN_2H_3O$ and $CsCN_2H_3O$ are largely similar with regard to the observed ADPs. By contrast, at ambient temperature the ADPs in the title anions are clearly smaller than those in urea, likely induced by the electrostatic attraction keeping the ureates more firmly in place.

Through the partial double-bond character between the atoms C and N2, the C–N2 bond is slightly shorter than C–N1, and a lengthening in the C=O bond is seen compared to the one in urea. No general difference could be seen between N–H bonds in the imino and amino group.

Despite formally exhibiting similar HB connectivity as the parent compound urea, the resulting HB network in $RbCN_2H_3O$ is quite different due to the influence of the metal cations. $CsCN_2H_3O$, again, is different from both: one observes not only HBs to the carbonyl oxygen atom,
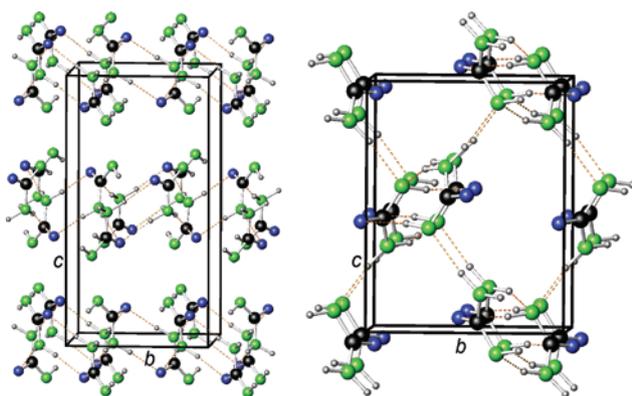
but also between hydrogen and nitrogen atoms, naturally leading to an HB network at variance with those in $RbCN_2H_3O$ and urea.

4 Experimental section

4.1 Synthesis of $RbCN_2H_3O$ and $CsCN_2H_3O$

Elementary Rb or Cs and equimolar amounts of freshly sublimed urea were placed into a steel autoclave which was then evacuated. After dry ammonia had been condensed into the autoclave, the latter was left sealed at $T = 50\,°C$ for 3 days. All further manipulations were carried out under inert conditions and followed previously described procedures [16].

4.2 X-ray diffraction

Initial structural models were derived from powder X-ray diffraction (P-XRD) experiments on both $RbCN_2H_3O$ and $CsCN_2H_3O$, using a STOE STADI P diffractometer ($CuK_{\alpha 1}$ radiation, $\lambda = 1.54059$ Å) equipped with a PSD detector. Data were collected in the 2θ range of $10–80°$ and refined using the Rietveld method as implemented in the FULL-PROF program package [29].

4.3 Neutron diffraction

Neutron powder diffraction measurements were performed on the time-of-flight powder diffractometer POWGEN located at the Spallation Neutron Source at Oak Ridge National Laboratory, Oak Ridge, TN (USA). Both $RbCN_2H_3O$ and $CsCN_2H_3O$ were measured at $T = 10$ and 300 K using two different wavelength bands, $\lambda_{center} = 1.333$ and 2.665 Å. For all measurements the POWGEN Automatic Sample Changer was used. To afford comparable statistics from the two different wavelength bands, the samples were measured for approximately 5.5 h at $\lambda_{center} = 1.333$ Å and for 3.5 h at 2.665 Å.

The collected neutron data were also refined by the Rietveld method using a pseudo-Voigt profile function with back-to-back exponentials and a linearly interpolated background between manually chosen points. Lattice parameters were refined using the above-described P-XRD experiments as starting point. Once refined lattice parameters from neutron diffraction had been obtained, these were taken as input for DFT computations which, together with the initial structural model, were used to compute

theoretically optimized values both for atomic sites and for all ADP matrix elements. Details of the DFT methodology are given below. The theoretical results were then fed back into the refinement process. "Soft restraints" with regard to interatomic distances were used to stabilize the refinement. In a last step, the background was smoothed by Fourier filtering using 1000 points. For $RbCN_2H_3O$, the refinements were carried out jointly for both wavelength bands. For $CsCN_2H_3O$, the reflection intensities were inferior in comparison, and thus these refinements were carried out separately for the two wavelength bands; results for $\lambda_{center} = 1.333$ Å are reported in the main text.

4.4 *Ab initio* computations

The crystal structures of both compounds derived from initial Rietveld refinements were subjected to *ab initio* simulations based on density-functional theory (DFT), aiming to obtain an initial model for the anisotropic thermal motion within the crystal structure. Such DFT-based predictions of ADPs have recently been validated against highly accurate single-crystal neutron diffraction experiments (including pure urea) [30] as well as temperature-dependent XRD [23].

DFT computations were performed using the projector augmented-wave method [31] as implemented in VASP [32–35]. The effects of electron exchange and correlation were modeled using the Perdew-Burke-Ernzerhof (PBE) functional [36], and the latter was augmented with dispersion corrections using Grimme's D2 scheme [37]. The cutoff energy for the plane-wave expansions was 500 eV. Reciprocal space was sampled on dense Monkhorst-Pack grids [38]. All atoms were fully relaxed within the constraints of space-group symmetry and the experimentally determined lattice vectors, and electronic (structural) cycles were halted upon reaching convergence within 10^{-8} (10^{-6}) eV, respectively.

ADPs were predicted based on phonon computations using PHONOPY [39, 40]. Thereby, forces on atoms were computed in $3 \times 3 \times 1$ ($3 \times 3 \times 2$) supercell expansions for Rb (Cs) ureate, respectively. The extraction of ADPs has been described, and their use validated, in the previous literature [23, 30, 41, 42]. Additional information on the computational procedures is provided via the Internet at http://www.ellipsoids.de.

4.5 Crystallographic data

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe,

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