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Synthesis and Crystal Structures of Two Metal Urea Nitrates

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Abstract $Cu(urea)_2(H_2O)_3(NO_3).(urea)(NO_3)$ (**1**) and $Zn(urea)_4(H_2O)_2 \cdot 2(NO_3)$ (**2**) have been obtained from the corresponding metal nitrates and urea in warm aqueous solvent. These are unusual examples of complexes of transition metals coordinated only by urea and water. **1** crystallizes in the monoclinic space group $P2_1/m$ with unit cell parameters $a = 9.489(3)$, $b = 13.059(3)$, $c = 7.103(2)$ Å and $\beta = 100.28(3)°$. The copper ion occupies a $2e$ position on a mirror plane and displays four short Cu–O bonds ($2 \times$ Cu–OH$_2$ and $2 \times$ Cu–O=C(NH$_2$)$_2$) and two much longer contacts (Cu–OH$_2$ and Cu–ONO$_2$) consistent with a Jahn–Teller distortion. Between the cations are located unbound urea and nitrate. **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.4239(11)$, $b = 17.690(4)$, $c = 7.5877(13)$ Å and $\beta = 91.138(14)°$. The zinc ion resides on the $2a$ position, an inversion centre, and displays pseudo–octahedral coordination geometry. It is coordinated by four equatorial urea and two axial water molecules. The four molecules of urea are nearly planar and form N–H···O intramolecular hydrogen bonds. Unbound charge-balancing nitrate is also present. In each compound there is extensive intermolecular hydrogen bonding between the water, urea, and nitrate present. Pyrolysis of the compounds under 10% hydrogen in nitrogen at 300 °C was found to yield metallic copper in the case of **1** and zinc oxide for **2**.

Keywords Urea · Carbamide · Coordination chemistry · Disorder · Hydrogen bonding

Introduction

Urea (carbamide (NH$_2$)$_2$C=O) has been extensively used in the generation of supramolecular solids, largely because of its facility in the formation of strong hydrogen bonds through donor (amine) and acceptor (carbonyl) functionalities. It is widely known as a host material for other small molecules [1, 2]. The formation of hydrogen-bonded extended solids based on urea has been reviewed recently [3]. Urea has also been found as a neutral ligand to metal cations, bound almost exclusively through the oxygen atom. This is a reflection of the unavailability of the amidic nitrogen lone pair and the value of the −NH$_2$ group for the formation of hydrogen bonds. Urea complexes frequently contain the ion M(urea)$_6^{n+}$ [4, 5] while the ion M(urea)$_4$(H$_2$O)$_2^{n+}$ [6, 7] is much less common. Gomathi [8] has shown that urea may be used as a nitriding source when mixed in excess with transition metal oxides. Thermal treatment is thought to yield ammonia which is the active nitriding species. Here we report two new metal urea nitrates, Cu(urea)$_2$(H$_2$O)$_3$(NO$_3$).(urea)(NO$_3$) (**1**) and Zn(urea)$_4$(H$_2$O)$_2 \cdot$2(NO$_3$) (**2**). The hydrogen bonding within their structures is discussed. Thermal treatment of these compounds and resulting products are also described.

Experimental

Synthesis

Reagents were purchased from Alfa Aesar and used without further purification. A 1:4 stoichiometric mixture of copper nitrate trihydrate (1.042 g, 4.313 mmol) and urea (1.035 g, 17.25 mmol) was dissolved in 70% aqueous ethanol (100 mL) with warming. This yielded blue crystals

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of **1** upon evaporation at room temperature. A similar procedure employing zinc nitrate hexahydrate (0.2566 g, 0.8626 mmol) and urea (0.2070 g, 3.45 mmol) in water yielded colorless crystals of **2**.

Thermal analysis: dry crystals were lightly ground in a pestle and mortar and placed inside an alumina boat. The boats were heated to 300 °C at a rate of 3 °Cmin^{-1} in a flow of 10% hydrogen in nitrogen and held there for 3 h. Analysis of each product was carried out by X-ray powder diffraction using a Siemens D5000 diffractometer operating with Cu Kα radiation.

X-ray Structure Determination

Single crystal X-ray diffraction data were collected using a Stoe IPDS2 image plate diffractometer operating with Mo radiation. Crystals were covered in a thin film of perfluoropolyether oil, mounted on a glass fiber, and cooled in an Oxford Instruments nitrogen gas cryostream. A unique set of data was obtained in each case using a series of ω-scans. Reflection intensities were integrated using standard procedures. In the case of **1**, the data were corrected for absorption using a multi-scan method based on equivalents [9]. Unit cell parameters were refined using all observed data. Structures were solved using routine automatic direct methods implemented with SHELXS [10]. Structures were completed by least squares refinement based on all unique measured F^2 values and difference Fourier methods implemented within the WinGX suite [11]. Basic data collection information is contained within Table 1.

In both structures data were of good quality and hydrogen atoms were located from difference Fourier maps and their positions refined. In **1**, all N–H bond lengths were restrained to be equal with a standard deviation of 0.03 Å. O–H bonds were restrained to 0.82(3) Å. For **2**, all chemically equivalent N–H and O–H bonds were restrained to be equal with a standard deviation of 0.03 Å. In each structure hydrogen atoms were refined using isotropic displacement parameters, with those which were chemically identical constrained to be equal. In **1** the nitrate disorder was modeled using isotropic displacement parameters. Chemically equivalent atoms in the two components were constrained to have the same displacement parameters. The two components were apparent from the difference Fourier maps. The occupancy of O3w was constrained to be the same as the major component. The refined ratio of the two components was 0.637(6):0.363(6).

The observed nitrate disorder in **1** is unexpected. To probe this further a second crystal was examined. This data collection was carried out at lower temperature in case the initial data collection had taken place close to a phase transition. The second crystal was slightly poorer quality, but affirmed the initial structure determination, in particular the presence of two nitrate orientations. Full details of the second structure determination are contained in the supplementary information. In neither set of data images was there evidence for additional spots which might indicate a larger true cell, for example a supercell corresponding to ordering of the nitrate.

In **1** the greatest peak in residual electron density is 1.08 eÅ^{-3} at 0.4187, 0.1824, 0.3434 (0.77 Å from O21A) and the deepest hole is −1.00 eÅ^{-3} at 0.4416, 0.2091, 0.4442 (0.56 Å from N20B). In **2** the greatest peak is 0.85 eÅ^{-3} at −0.0019, 0.0600, 0.9869 (1.07 Å from Zn1) and the deepest hole is −1.31 eÅ^{-3} at 0.0769, 0.0007, 0.9148 (0.82 Å from Zn1).

Results and Discussion

There is significant disorder in the species bound to the Cu^{2+} cation in **1**. The *ORTEP* diagram in Fig. 1 shows the coordination about the copper ion with the major form highlighted, which has composition [Cu(urea)$_2$(H$_2$O)$_3$NO$_3$]·(urea)(NO$_3$). In the major orientation, the coordination number of the Cu^{2+} is six; the planar arrangement of four oxygen donors (two urea and two water molecules in a *trans* fashion) is augmented by two other ligands with longer Cu–O distances (Table 2). The heavily distorted octahedral geometry about Cu1 is completed by loosely-bound water (O3w; Cu–O is 2.441 (6) Å) and monodentate nitrate (N20A, O20A, O21A; Cu–O20A is 2.577 (6) Å). The [4 + 2] coordination is in line with that predicted for the Jahn–Teller active d^9 ion Cu^{2+}. Fourier maps around the nitrate, calculated when all other non-hydrogen atoms had been located, categorically indicated the presence of a second orientation for this nitrate. In the minor form the nitrate is present in a second orientation related to the first by a displacement of 0.491(15) Å and a rotation of approximately 60° so that it no longer binds to the copper. In this position there is excessively close approach of O20B and O3w of an adjacent ion. This, coupled with an anomalously large displacement parameter for O3w when it is fully occupied, suggests partial occupancy: O3w is only present when the nitrate is present in the major orientation. This is reinforced by the formation of two hydrogen bonds from H3A and H3B to O21A in an adjacent molecule. The major orientation of nitrate and bound water is 63.7(6)% occupied. In the minor form the change in nitrate orientation and hydration yields this formula, [Cu(urea)$_2$(H$_2$O)$_2$]·2(NO$_3$)(urea). The Cambridge Structural Database (CSD, version 5.29) [12] reveals that the net square planar, four coordination of Cu^{2+} present in the minor orientation is not uncommon for copper bound by four oxygen donor ligands. There was no evidence in the diffraction images in the form of extra spots to suggest ordering of the nitrate. The four short Cu–O bonds lie at the shorter end of the range expected for

Table 1 Summary of crystal data for **1** and **2**

Identification code	**1**	**2**
Empirical formula	C4 H21.27 Cu N10 O12.64	C4 H20 N10 O12 Zn
Formula weight	475.33	465.65
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/n$
Unit cell dimensions	$a = 9.489(3)$ Å $\alpha = 90°$	$a = 6.4239(11)$ Å $\alpha = 90°$
	$b = 13.059(3)$ Å $\beta = 100.28(3)°$	$b = 17.690(4)$ Å $\beta = 91.138(14)°$
	$c = 7.103(2)$ Å $\gamma = 90°$	$c = 7.5877(13)$ Å $\gamma = 90°$
Volume	866.1(4) Å^3	862.1(3) Å^3
Z	2	2
Density (calculated)	1.823 Mg/m^3	1.794 Mg/m^3
Absorption coefficient	1.351 mm^{-1}	1.509 mm^{-1}
F(000)	490.7	480
Crystal size	$0.3 \times 0.3 \times 0.1$ mm^3	$0.3 \times 0.1 \times 0.1$ mm^3
Theta range for data collection	2.68–27.00°	2.30–29.58°
Index ranges	$-12 \leq h \leq 12, -16 \leq k \leq 16, -9 \leq l \leq 8$	$-8 \leq h \leq 8, -23 \leq k \leq 24, -10 \leq l \leq 10$
Reflections collected	9,707	6,891
Independent reflections	1,968 [R(int) = 0.0774]	2,363 [R(int) = 0.0763]
Completeness to theta = 27.00°	99.9%	98.0%
Absorption correction Max. and min. transmission	Semi-empirical from equivalents. 0.873 and 0.737	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1,968/33/171	2,363/34/156
Goodness-of-fit on F^2	0.973	0.930
Final R indices [I > 2sigma(I)]	R1 = 0.0460, wR2 = 0.1098	R1 = 0.0353, wR2 = 0.0791
R indices (all data)	R1 = 0.0729, wR2 = 0.1203	R1 = 0.0549, wR2 = 0.0844
Largest diff. peak and hole	1.075 and -0.998 eÅ^{-3}	0.848 and -1.314 eÅ^{-3}

Table 2 Selected bond lengths for **1** and **2**

1		**2**	
Cu1–O1W	1.930(4)	Zn1–O1	2.0892(14)
Cu1–O2W	1.931(4)	Zn2–O2	2.0754(15)
Cu1–O1^i	1.938(2)	Zn1–O2^{ii}	2.0754(15)
Cu1–O1	1.938(2)	Zn1–O1^{ii}	2.0892(14)
O1–C1	1.273(4)	Zn1–O1w	2.1446(16)
N1–C1	1.322(4)	Zn1–O1w^{ii}	2.1446(16)
N2–C1	1.329(4)	C1–O1	1.259(3)
		C1–N2	1.330(3)
		C1–N1	1.344(3)
		C2–O2	1.258(2)
		C2–N4	1.330(3)
		C2–N3	1.346(3)

Symmetry transformations used to generate equivalent atoms: i = x, $-y + 1/2$, z; ii = $-x$, $-y$, $-z$

Cu–O distances from the CSD but are in good agreement with those in Cu(urea)$_4$(NO$_3$)$_2$ [6]. It is notable that equivalent C=O and C–N bonds in the bound and free urea molecules do not differ significantly in length.

The [Cu(urea)$_2$(H$_2$O)$_3$NO$_3$]$^+$ ion in **1** has an extensive capacity to hydrogen bond through urea, water and nitrate. In addition to this, the structure is completed by unbound urea and nitrate which are also engaged in hydrogen bonding. Details of hydrogen bonds within **1** are contained in Table 3. One way of describing the structure is in terms of the hydrogen bonded layers present, the principal interactions forming these, and the interactions between them [13]. For each nitrate orientation $C_2^2(12)$ chains parallel to the [101] direction form from bound urea molecules on adjacent copper ions. Parallel to these are $C_2^2(10)$ chains between free nitrate and bound urea. $C_3^3(10)$ chains involving the nitrate and cations lie parallel to the [010] direction. These interactions lead to hydrogen bonded sheets (illustrated in Fig. 2) and from these project bound
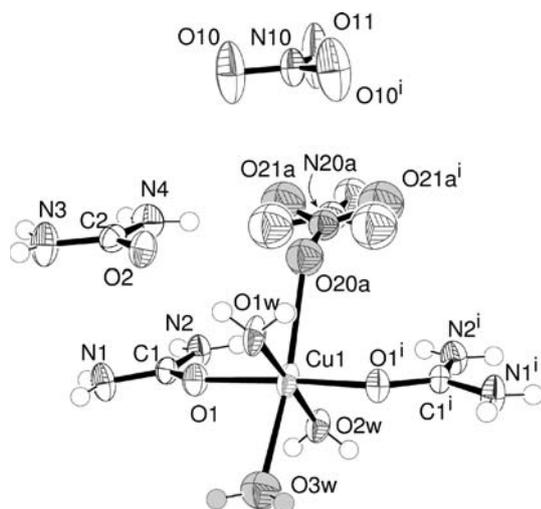
Fig. 1 Coordination about the copper ion in **1** with atoms drawn as 70% thermal ellipsoids. The major (63.7%) nitrate orientation is shaded; O3w is also 63.7% occupied. The minor nitrate orientation (unshaded) is 36.3% occupied. All other atoms are full occupied. [Symmetry code: (i) x, $1/2-y$, z]

Fig. 2 Part of a hydrogen-bonded sheet in **1**. C_2^2 (12) chain parallel to [101] is labeled A. The C_3^3 (10) chain parallel to [010] is labeled B

Fig. 3 Hydrogen bonding between unbound urea and nitrate in **1**, shown as single dashed lines, assembles these into sheets. Interlayer hydrogen bonds are marked with double dashed lines

Table 3 Hydrogen bonds in **1** [Å and °]

D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	<(DHA)
O1w-H1⋯O2	0.79(4)	1.91(4)	2.674(4)	162(5)
N1-H1A⋯O1^i	0.83(3)	2.17(3)	2.990(4)	177(6)
N1-H1B⋯O2^{iii}	0.83(4	2.06(4)	2.883(4)	173(3)
O2w-H2⋯O2^{iii}	0.79(4)	1.91(4)	2.705(4)	175(4)
N2-H2A⋯O10^{iii}	0.82(3)	2.22(5)	2.905(4)	141(4)
N2-H2B⋯O10^{iv}	0.82(3)	2.30(3)	3.118(4)	173(5)
N3-H3A⋯O2^v	0.83(4)	2.17(3)	2.985(4)	171(4)
N3-H3B⋯O3W^{vi}	0.83(4)	2.56(4)	2.925(5)	108(3)
O3W-H3C⋯O21A^{vii}	0.88(3)	2.46(5)	3.123(10)	132(3)
N4-H4A⋯O20A	0.83(3)	2.41(3)	3.208(5)	163(4)
N4-H4B⋯O21A^{iv}	0.83(4)	2.10(3)	2.887(8)	160(4)

Symmetry transformations used to generate equivalent atoms

i = $-x + 2$, $-y$, $-z + 1$; ii = $-x + 1$, $y-1/2$, $-z + 1$; iii = x, y, $z-1$; iv = $-x + 1$, $-y$, $-z + 1$; v = $-x + 2$, $-y$, $-z + 2$; vi = $-x + 2$, $y-1/2$, $-z + 1$; vii = $x + 1$, y, z

water and nitrate (N20a). Between these sheets are further hydrogen bonded sheets formed from the unbound urea and nitrate. In the major orientation of the disordered nitrate, hydrogen bonding in these layers is dominated by $R_2^2(8)$ dimers of urea and the nitrate is set at an angle of approximately 25.8° to the plane of the layer. However, in the minor orientation, nitrate now resides in approximately the same plane as the unbound urea which leads to the formation of a 2-D hydrogen bonding array of urea and nitrate. The two sets of layers are stacked in ABAB fashion along the [101] direction. Hydrogen bonds between water, nitrate, and unbound urea knit these layers together to
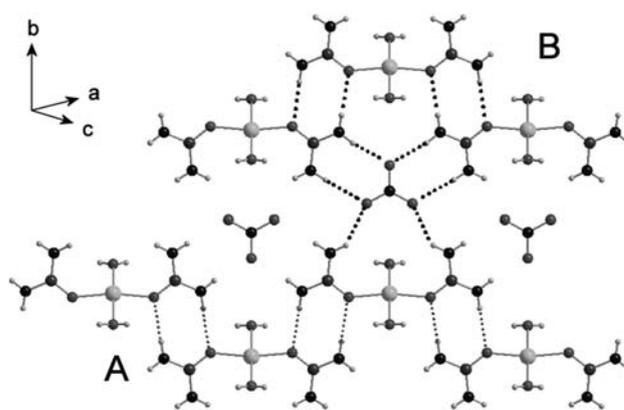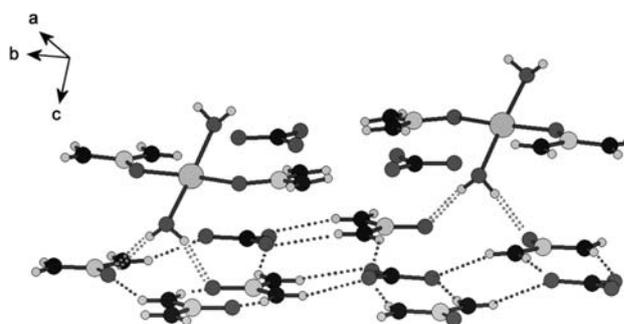
generate a three dimensional array. For the minor orientation, the nitrate (N20b) is now located in the free urea layer and reinforces the hydrogen bonding there; interlayer-hydrogen bonding is now only due to water-urea interaction. Figure 3 illustrates the two types of hydrogen bonded layer and the interaction between them.

The disorder of the loosely-bound nitrate is interesting but occurs for very clear chemical reasons. In the major orientation, the favorable binding of nitrate by Cu^{2+} is augmented by hydrogen bonding, in particular to the hydrogen atoms attached to O3w. However, the long Cu–O distances indicate this is a rather weak interaction, hence the existence of the second nitrate orientation. For the minor orientation, the nitrate forms a different set of N–H⋯O interactions, reinforcing hydrogen bonding between the unbound urea molecules. The observed disorder is not a function of the individual crystal studied, but a property of the sample. Examination of the structure of a second crystal of the material showed a very similar distribution of the two orientations of nitrate. The two forms are obviously relatively close in energy.

$Zn(urea)_4(H_2O)_2 \cdot 2(NO_3)$ is isostructural with the nickel and cobalt analogues. No disorder is present in this phase.

Table 4 Hydrogen bonds in **2** [Å and °]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O1w-H1···O4[ii]	0.80(3)	2.03(3)	2.806(2)	168(3)
N1-H1A···O3[iii]	0.85(2)	2.23(2)	3.065(3)	170(2)
N1-H1B···O3[iv]	0.83(3)	2.30(3)	3.085(3)	158(3)
O1w-H2···O5[v]	0.83(3)	2.07(3)	2.882(2)	167(4)
N2-H2A···O2[i]	0.85(2)	2.11(3)	2.845(3)	144(3)
N2-H2A···O5[ii]	0.85(2)	2.59(3)	3.124(3)	122(2)
N2-H2B···O5[iii]	0.85(2)	2.14(2)	2.983(3)	177(3)
N3-H3A···O1w[vi]	0.85(2)	2.25(2)	3.092(3)	170(2)
N3-H3B···O3	0.86(2)	2.24(2)	3.096(3)	176(2)
N4-H4A···O1	0.85(2)	2.04(2)	2.813(3)	151(3)
N4-H4B···O4	0.85(2)	2.38(2)	3.225(3)	168(3)

Symmetry transformations used to generate equivalent atoms

i = $-x$, $-y$, $-z$; ii = $-x + 1/2$, $y-1/2$, $-z-1/2$; iii = $x-3/2$, $-y + 1/2$, $z-1/2$; iv = $x-1$, y, z; v = $x-1/2$, $-y + 1/2$, $z-1/2$ vi = $-x + 1$, $-y$, $-z$

An elegant description of the Ni and Co analogues has already appeared [7]. Here the structure is described briefly and its relation to $Cu(urea)_2(H_2O)_3(NO_3)\cdot(urea)(NO_3)$ is highlighted. The structure is composed of $[Zn(urea)_4 (H_2O)_2]^{2+}$ units, in which the water ligands are *trans*, and charge balancing unbound nitrate. The four urea ligands are approximately planar and form a $R_4^4(16)$ ring of intramolecular hydrogen bonds (N–H···O=C). (Fig. 4) The Zn–O bond lengths are similar to those reported for the Co and Ni analogues, although longer, as expected, due to the larger ionic radius of Zn^{2+} [14]. These bond lengths lie in the middle of the range for similar compounds on the CSD in which urea binds to Zn^{2+} (Table 2). The C=O bond lengths in urea are in agreement with those found in other first row transition metal complexes of urea contained in the CSD which are clustered around 1.25 Å. Hydrogen bonding (Table 4) between urea, water, and nitrate assembles these
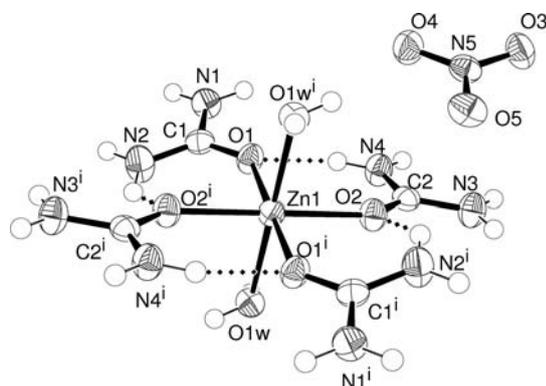

Fig. 4 Coordination about the zinc ion in **2** with atoms drawn as 70% thermal ellipsoids. Intramolecular hydrogen bonds are drawn as dotted lines. [Symmetry code: (i) $-x$, $-y$, $-z$]
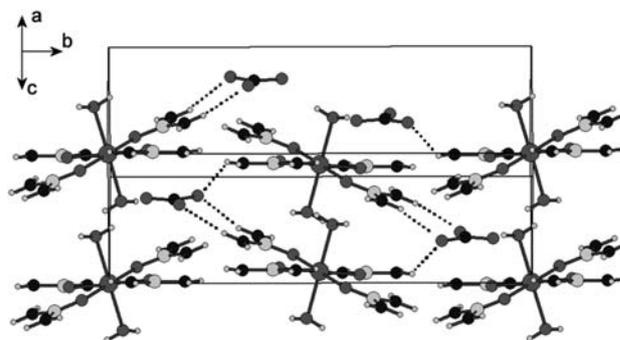

Fig. 5 Three stacks formed between $[Zn(urea)_4(H_2O)_2]^{2+}$ cations and nitrate. Weak inter-stack hydrogen bonds are shown as dotted lines

$[Zn(urea)_4(H_2O)_2]^{2+}$ ions into stacks which are one extended cation wide and extended parallel to [001]. These are illustrated in Fig. 5. Between the stacks are longer, weaker, urea—nitrate hydrogen bonds (N3···O3 is 3.096 (3) Å; N4···O4 is 3.225 (3) Å; N1[i]···O3 is 3.085 (3) Å, where $i = 1 + x$, y, z). Note that the inter-stack hydrogen bonds are due to nitrate acting as an acceptor and these are rather weak. The urea molecule preferentially forms pairs of strong reciprocal urea C=O···H–N bonds.

Structural similarities between **1** and **2** stem from the existence of strong intermolecular hydrogen bonds which assemble individual components into distinct structural units which are knit together into a three dimensional array by further hydrogen bonds. In **1**, extensive hydrogen bonding gives 2-D sheets which are linked by further hydrogen bonds. Note that in the minor orientation hydrogen bonding within one layer is strengthened (urea nitrate layer) while the interlayer interaction is weakened. For **2**, strong hydrogen bonds direct the coordination about the zinc cation and intermolecular interactions assemble these extended cations and nitrate into stacks, which are loosely held into a 3-D arrangement. The ultimate aim of this work was to obtain metal-urea complexes of well determined stoichiometry. Urea is known to be a source of ammonia when it undergoes thermal decomposition. The presence of urea bound at the metal suggested that thermolysis of these compounds might convert them to metal nitrides with only gaseous byproducts. Thermolysis of each compound at 300 °C did not yield the desired product but copper metal and zinc oxide.

Supplementary Material

CCDC 704905 and 704906 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(0)1223-336033.

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