

Hydrogen bonding in diaquatetrakis-(urea- κ O) M^{II} dinitrates, with $M = \text{Ni}$ and Co

Anna Krawczuk* and Katarzyna Stadnicka

 Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland
 Correspondence e-mail: krawczuk@chemia.uj.edu.pl

Received 7 August 2007

Accepted 14 August 2007

Online 22 September 2007

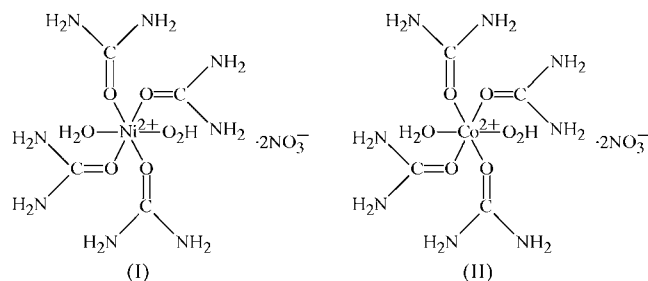
The isomorphous title compounds, $[\text{Ni}\{(\text{NH}_2)_2\text{CO}\}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ and $[\text{Co}\{(\text{NH}_2)_2\text{CO}\}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$, feature discrete centrosymmetric cations in octahedral coordinations, formed by four urea molecules linked *via* their O atoms to the central ion in equatorial positions and two water molecules in *trans* positions. The complexes are packed in a pseudo-hexagonal manner separated by the nitrate counter-ions. All H atoms are involved in moderate hydrogen bonds of four types: $\text{N}-\text{H}\cdots\text{O}=\text{C}$, $\text{N}-\text{H}\cdots\text{O}-\text{N}$, $\text{O}-\text{H}\cdots\text{O}-\text{N}$ and $\text{N}-\text{H}\cdots\text{O}-\text{H}$. Graph-set analysis was applied to distinguish the hydrogen-bond patterns at unitary and higher level graph sets.

Comment

Urea plays an important role in crystal engineering. Possessing both donor and acceptor functional groups (one carbonyl and two amino groups), it can form rich hydrogen-bond networks. Due to lone electron pairs on the N and O atoms, urea can also coordinate to metal ions through either N or O. Several nickel(II) and cobalt(II) complexes containing more than two urea molecules in the coordination environment are found in the Cambridge Structural Database (CSD, Version 5.28 of 2006; Allen, 2002) with refcodes ADUFEK (Rybak-Akimova *et al.*, 2002), FOWQIR (Kuzmina *et al.*, 2000), NIURC (Suleimanov *et al.*, 1971), COLLAQ (Suleimanov *et al.*, 1984), FADGEX (Kuzmina *et al.*, 2001) and FOWQOX (Kuzmina *et al.*, 2000). They consist mainly of discrete $M(\text{urea})_6$ cations, one additional free urea molecule per cation, and counter-ions such as Cl^- , Br^- , I^- , I_3^- and NO_3^- .

We report here the crystal structures of the isostructural title complexes, diaquatetraureanickel(II) dinitrate, (I), and diaquatetraureacobalt(II) dinitrate, (II). The crystal structure of (II), previously reported by Rau & Kurkutova (1971), was redetermined because of the high *R* factor (0.192) and lack of H atoms in the earlier work. The presence of numerous hydrogen bonds in (I) and (II) results in characteristic arrays which may be described by graph-set analysis according to Etter *et al.* (1990) and Bernstein *et al.* (1995).

The centrosymmetric complex cation of (I) consists of four urea molecules coordinated *via* O atoms to the Ni^{II} central



atom in equatorial positions and two water molecules in *trans* positions. The coordination polyhedron is a near-perfect octahedron, with angular deviations of less than 0.5° . The positive charge of the Ni cation is balanced by two nitrate anions, as shown in Fig. 1. The urea $\text{C}=\text{O}$ bond lengths (Table 1) are shortened and the $\text{C}-\text{N}$ bonds ($\text{C1}-\text{N1}$ and $\text{C2}-\text{N4}$) are elongated in both symmetry-independent molecules. The shortening of the $\text{C}=\text{O}$ bond lengths is caused by two functions of the O atom: it acts as an acceptor in intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and, at the same time, as the ligand to the central cation. The elongation of the urea $\text{C}-\text{N}$ bond lengths is induced by the strong acceptor properties of the O atoms of the nitrate groups in intermolecular hydrogen bonds of the $\text{N}-\text{H}\cdots\text{O}-\text{N}$ type. The packing in (I) viewed along $[100]$ is shown in Fig. 2. The discrete coordination polyhedra are packed in a pseudo-hexagonal pattern and are separated by nitrate anions.

For both structures, the geometric parameters of the urea molecules are equal within the limits of error, whereas the $M-\text{O}$ bond lengths of (I) are relatively short compared with those of (II), which is caused by the difference in the Ni^{2+} and Co^{2+} ionic radii (Shannon, 1976). The differences in $M-\text{O}$ bond lengths are typical for all structures quoted from the CSD.

All H atoms participate in hydrogen bonds, which can be classified into four types by functional group: (a) $\text{N}-\text{H}\cdots\text{O}=\text{C}$, (b) $\text{N}-\text{H}\cdots\text{O}-\text{N}$, (c) $\text{O}-\text{H}\cdots\text{O}-\text{N}$ and (d) $\text{N}-$

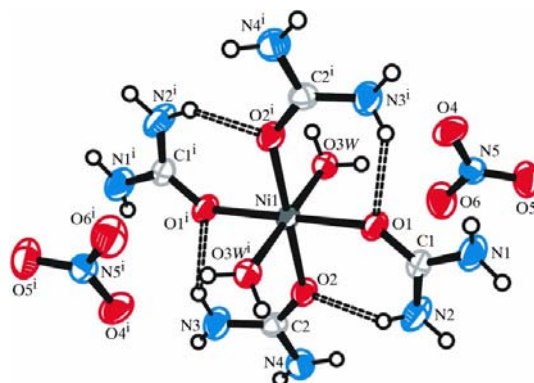


Figure 1
 A view of compound (I), showing the atom-labelling scheme. Intramolecular hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Compound (II) is isomorphous. [Symmetry code: (i) $-x, -y, -z$.]

H···O—H. For the network of observed hydrogen bonds, graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995) was applied, taking into account unitary, binary and ternary graph sets.

The unitary graph sets (N_1) are shown in Fig. 3. Patterns for (a), (b) and (c) type hydrogen bonds are in the same layer, perpendicular to $[\bar{1}01]$. Inside the complex cation, there is an $R_4^4(16)$ motif built of N—H···O=C hydrogen bonds [*i.e.* type (a)]. The patterns consisting of type (b) hydrogen bonds can be described as ring arrays. However, the hydrogen bonds are not crystallographically equivalent, so the pattern should have a DD descriptor assigned, which on the binary graph level converts to an $R_2^2(8)$ descriptor. A similar situation is observed in the case of type (c) bond patterns. The motifs composed of bifurcated hydrogen bonds between water molecules and

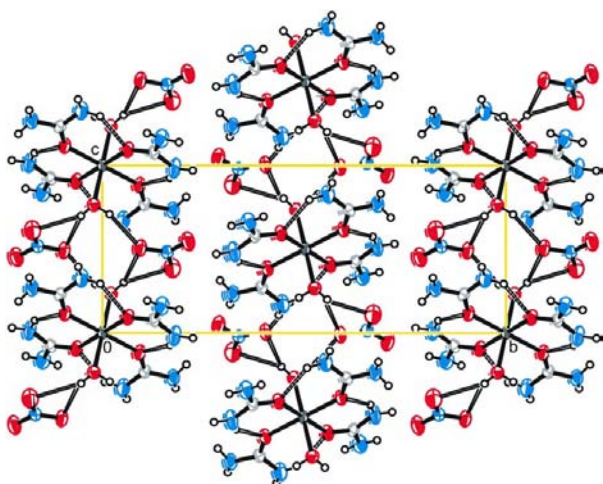


Figure 2
The pseudo-hexagonal packing in the structure of (I), viewed along the a axis. Some of the hydrogen bonds are shown, *viz.* N—H···O=C as dashed bonds and O—H···O—N as open bonds. Displacement ellipsoids are drawn at the 30% probability level.

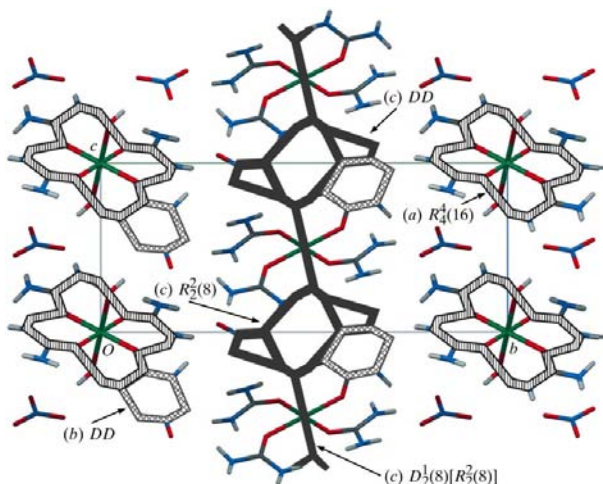


Figure 3
Graph-set assignment of the unitary level for (I); the same assignment is valid for (II). Different hydrogen-bond patterns are distinguished by different graphical symbols and defined by specific descriptors. (a) N—H···O=C shaded; (b) N—H···O—N cross-hatched; (c) O—H···O—N dark grey.

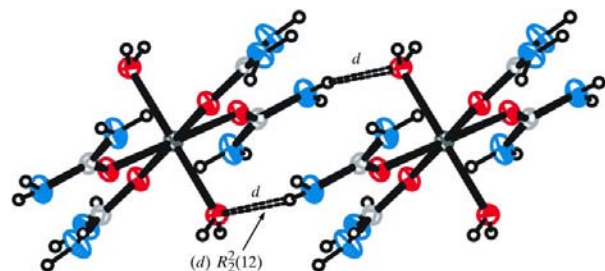


Figure 4
The hydrogen-bond pattern composed of type (d) hydrogen bonds (N—H···O—H).

nitrate anions have DD descriptors on the first-level graph set and $R_1^1(4)$ on the second-level graph set. For type (c) hydrogen bonds, one can also distinguish an $R_2^2(8)$ ring at the unitary level and an $R_4^4(12)$ ring, which can be obtained by assembling three rings, two $R_2^2(4)$ and one $R_2^2(8)$.

Additionally, there is a motif composed of type (c) hydrogen bonds which occurs as a ‘chain of rings’, having descriptor $D_2^1(8)[R_2^2(8)]$, which describes the chain along the $[001]$ direction with only one branch of the $R_2^2(8)$ ring included. The motif built of type (d) hydrogen bonds, in the form of an $R_2^2(12)$ ring, is shown in Fig. 4; it joins neighbouring layers perpendicular to $[\bar{1}01]$ into a three-dimensional structure. Higher level graph sets, not marked in the figures, can also be defined. Among them there are, for example, a $D_4^4(16)$ binary graph set (N_2) built with (a) and (b) type hydrogen bonds, and a $D_4^4(20)$ third-level graph set (N_3) formed by (a), (b) and (c) type hydrogen bonds. The quantitative descriptors of hydrogen-bond patterns at the unitary and binary graph set levels, identical for the isostructural crystalline phases of (I) and (II), are given in Table 3.

In conclusion, the most important description seems to be that of the first-level graph sets (motifs), as, in general, assembling the unitary graph sets provides the patterns consisting of a few hydrogen-bond types which are then described by higher level graph sets.

Experimental

Nickel(II) nitrate hexahydrate was dissolved in hot propan-2-ol under reflux, to which crystalline urea was added. The molar ratio of nickel salt to urea was 1:4. The solution was filtered and then left to evaporate slowly at room temperature. Green crystals of (I) were obtained after a few weeks. Diaquatetraureacobalt(II) dinitrate, (II), was obtained by spontaneous recrystallization of tetraureacobalt(II) dinitrate (Gentile *et al.*, 1974) in the presence of a trace amount of water.

Compound (I)

Crystal data

$[\text{Ni}(\text{CH}_4\text{N}_2\text{O})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$	$V = 873.79$ (5) \AA^3
$M_r = 459.01$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.4580$ (2) \AA	$\mu = 1.19$ mm^{-1}
$b = 18.0522$ (5) \AA	$T = 293$ (2) K
$c = 7.5331$ (3) \AA	$0.50 \times 0.48 \times 0.35$ mm
$\beta = 95.758$ (2)°	

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.569$, $T_{\max} = 0.660$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.04$
1950 reflections
124 parameters

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond lengths (Å) for (I).

Ni1—O1	2.060 (1)	O2—C2	1.252 (2)
Ni1—O2	2.064 (1)	C2—N3	1.326 (3)
Ni1—O3W	2.082 (1)	C2—N4	1.340 (2)
O1—C1	1.254 (2)	N5—O6	1.231 (2)
C1—N2	1.319 (3)	N5—O5	1.243 (2)
C1—N1	1.340 (2)	N5—O4	1.256 (2)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O3W ⁱ	0.87	2.32	3.185 (2)	168
N1—H1B \cdots O5 ⁱⁱ	0.88	2.25	3.125 (2)	172
N2—H2A \cdots O6 ⁱⁱ	0.88	2.33	3.188 (2)	167
N2—H2B \cdots O2	0.88	2.03	2.814 (2)	148
N3—H3A \cdots O1 ⁱⁱⁱ	0.88	2.04	2.815 (2)	146
N3—H3B \cdots O4 ^{iv}	0.88	2.20	3.062 (3)	165
N4—H4A \cdots O5 ^v	0.88	2.26	3.101 (3)	162
N4—H4B \cdots O5 ^{iv}	0.88	2.16	3.031 (2)	173
O3W—H1W \cdots O4 ^{vi}	0.83	2.08	2.884 (2)	163
O3W—H2W \cdots O4	0.83	2.21	2.987 (2)	156
O3W—H2W \cdots O6	0.83	2.26	2.996 (2)	147

Symmetry codes: (i) $x+1, y, z$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $x-1, y, z-1$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (vi) $-x, -y, -z+1$.

Compound (II)

Crystal data

$[\text{Co}(\text{CH}_4\text{N}_2\text{O})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 $M_r = 459.23$
Monoclinic, $P2_1/n$
 $a = 6.4655 (2) \text{ Å}$
 $b = 17.9321 (5) \text{ Å}$
 $c = 7.6201 (2) \text{ Å}$
 $\beta = 94.428 (1)^\circ$

$V = 880.84 (4) \text{ Å}^3$
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.06 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 $0.32 \times 0.32 \times 0.20 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.729$, $T_{\max} = 0.816$

8072 measured reflections
2661 independent reflections
2133 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.082$
 $S = 1.04$
2661 reflections

124 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{Å}^{-3}$

Table 3

Quantitative graph-set descriptors of the first and second levels for structures (I) and (II).

Hydrogen-bond types: (a) $\text{N}-\text{H}\cdots\text{O}=\text{C}$; (b) $\text{N}-\text{H}\cdots\text{O}-\text{N}$; (c) $\text{O}-\text{H}\cdots\text{O}-\text{N}$; (d) $\text{N}-\text{H}\cdots\text{O}-\text{H}$.

Hydrogen-bond type	(a)	(b)	(c)	(d)
(a)	$R_4^+(16)$			
(b)	$D_4^+(16)$	$DD, R_2^2(8)$		
(c)			$R_2^2(8), R_1^1(4), D_2^1(8)[R_2^2(8)]$	
(d)				$R_2^2(12)$

The H atoms of the water molecules and urea amino groups were found in difference Fourier maps and refined in a riding model, with $\text{O}-\text{H} = 0.84 \text{ Å}$ and $\text{N}-\text{H} = 0.88 \text{ Å}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom.

For both compounds, data collection: COLLECT (Nonius, 2000); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003), ORTEP-3 for Windows (Farrugia, 1997) and Mercury (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

The authors thank the Joint X-ray Laboratory, Faculty of Chemistry, Jagiellonian University, for making the Nonius KappaCCD diffractometer available.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3094). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gentile, P. S., White, J. & Haddad, S. (1974). *Inorg. Chim. Acta*, **8**, 97–103.
- Kuzmina, N. E., Palkina, K. K., Savinkina, E. V., Biryukov, D. A. & Kozlova, I. A. (2001). *Zh. Neorg. Khim.* **46**, 1324–1331.
- Kuzmina, N. E., Palkina, K. K., Savinkina, E. V., Kuznetsov, N. T. & Kozlova, I. A. (2000). *Zh. Neorg. Khim.* **45**, 780–789.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nonius (2000). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Rau, T. F. & Kurkutova, E. N. (1971). *Dokl. Akad. Nauk SSSR*, **200**, 1340–1342.
- Rybak-Akimova, E. V., Kryatov, S. & Robinson, P. D. (2002). Private communication.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Suleimanov, Kh., Antsyshkina, A. S., Dudarev, V. Ya., Fykin, L. V. & Porai-Koshits, M. A. (1984). *Koord. Khim. (Russ.)*, **10**, 1272–1278.
- Suleimanov, Kh., Porai-Koshits, M. A., Antsyshkina, A. S. & Sulaimankulov, K. (1971). *Zh. Neorg. Khim.* **16**, 3394–3396.