

Diaquabis(biuretato- $\kappa^2O,O'$ )nickel(II) dichlorideJeffrey Lawson and  
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## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{N}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.047  
 $wR$  factor = 0.101  
Data-to-parameter ratio = 23.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2$ , contains  $\text{Ni}^{2+}$  cations octahedrally coordinated by two bidentate biuret molecules in an  $O,O'$ -bidentate coordination mode and two water molecules, the latter in a *trans* configuration. Two chloride anions provide charge compensation. Numerous  $\text{N}-\text{H}\cdots\text{O}$  (mean  $\text{H}\cdots\text{O} = 2.17$  Å, mean  $\text{N}-\text{H}\cdots\text{O} = 164^\circ$  and mean  $\text{N}\cdots\text{O} = 2.991$  Å),  $\text{N}-\text{H}\cdots\text{Cl}$  (mean  $\text{H}\cdots\text{Cl} = 2.46$  Å, mean  $\text{N}-\text{H}\cdots\text{Cl} = 162^\circ$  and mean  $\text{N}\cdots\text{Cl} = 3.278$  Å) and  $\text{O}-\text{H}\cdots\text{Cl}$  (mean  $\text{H}\cdots\text{Cl} = 2.19$  Å, mean  $\text{O}-\text{H}\cdots\text{Cl} = 159^\circ$  and mean  $\text{O}\cdots\text{Cl} = 3.068$  Å) hydrogen bonds help to stabilize the crystal packing.

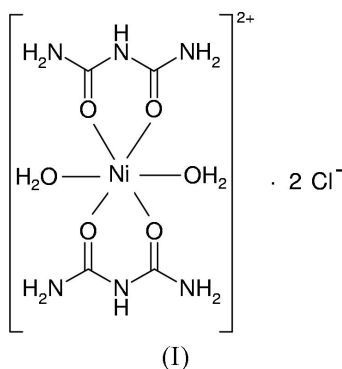
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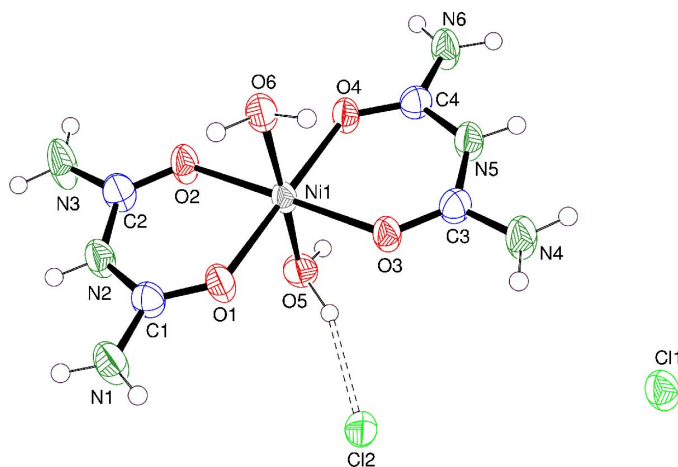
Online 12 February 2005

## Comment

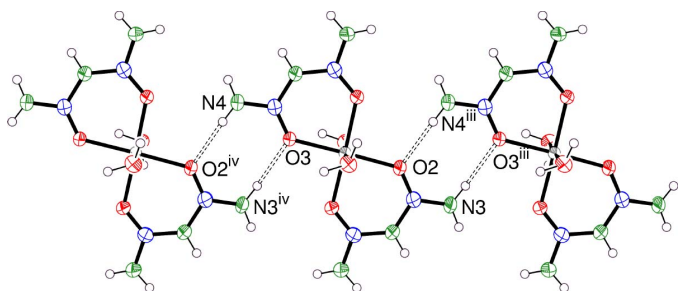
Biuret,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CO}-\text{NH}_2$  (or  $\text{C}_2\text{H}_5\text{N}_3\text{O}_2$ ), has long been recognized as a ligand in coordination chemistry (Wiedemann, 1848). In low-pH or neutral conditions, biuret commonly shows  $O,O'$ -bidentate coordination to metal cations [*e.g.* with zinc (Nardelli *et al.*, 1963), copper (Freeman & Smith, 1966) or samarium (Haddad, 1987)]. When biuret is deprotonated in basic conditions,  $N,N'$ -bidentate coordination can arise [*e.g.* with copper (Pajunen & Pajunen, 1982)].



In the present paper, we report the synthesis and structure of a nickel(II) complex of biuret, *viz.*  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2$ , (I) (Fig. 1). Compound (I) contains  $\text{Ni}^{2+}$  cations coordinated by two distinct biuret molecules, in  $O,O'$ -bidentate mode (thus forming six-membered chelate rings), and two *trans* water molecules. The structure is completed by two uncoordinated chloride ions, which provide charge balance and participate in an extensive hydrogen-bond network (see below). The resulting  $\text{NiO}_6$  moiety of the  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_2(\text{H}_2\text{O})_2]^{2+}$  grouping (Table 1) is close to being an undistorted octahedron [ $\text{Ni}-\text{O} = 2.014$  (2)– $2.083$  (2) Å, mean


**Figure 1**

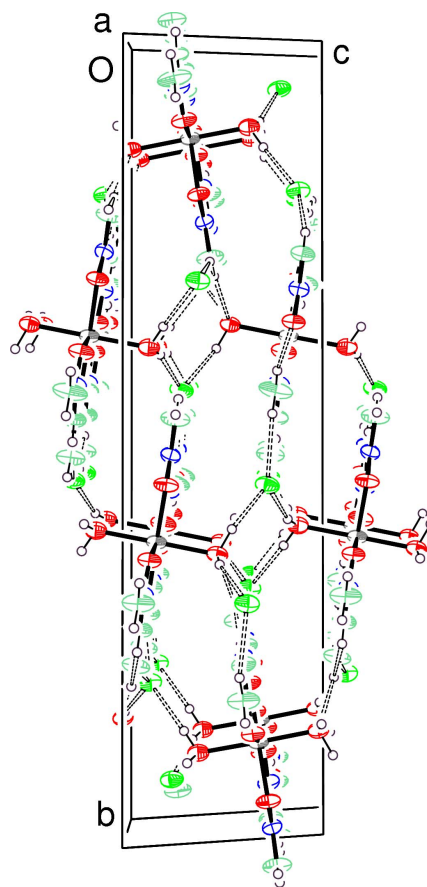
Asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and the hydrogen bond is indicated by dashed lines.


**Figure 2**

Detail of (I), showing how the  $N3-H4 \cdots O3^{iii}$  and  $N4-H6 \cdots O2^{iv}$  hydrogen bonds (dashed lines; see Table 2 for symmetry codes) link the  $[Ni(C_2H_5N_3O_2)_2(H_2O)_2]^{2+}$  groupings into an infinite chain propagating along [100].

$Ni-O = 2.041(3) \text{ \AA}$ ; *cis* and *trans*  $O-Ni-O = 87.47(9)-93.51(8)^\circ$  and  $176.14(9)-178.94(8)^\circ$ , respectively], indicating that the nickel(II) cation is a good 'fit' for the biuret  $O, O'$  bite angle. The two biuret molecules in (I) can be broken down into two  $H_2N-CO-NH$  fragments, fused *via* the central HN group [*i.e.* *via* atoms N2 and N5 in (I)]. For the non-H atoms, the four  $H_2N-CO-NH$  fragments are all essentially planar (for C1/O1/N1/N2, r.m.s. deviation from the least-squares plane =  $0.0021 \text{ \AA}$ ; for C2/O2/N2/N3,  $0.0017 \text{ \AA}$ ; for C3/O3/N4/N5,  $0.0023 \text{ \AA}$ ; for C4/O4/N5/N6,  $0.0032 \text{ \AA}$ ). The dihedral angle between the C1- and C2-containing fragments is  $4.8(3)^\circ$ , with a corresponding value of  $3.19(3)^\circ$  for the C3 and C4 fragments. This configuration can be compared with a twist angle between the fused  $H_2N-CO-NH$  fragments of  $6.35^\circ$  in  $[Cu(C_2H_5N_3O_2)_2]Cl_2$  (Freeman & Smith, 1966). The dihedral angle between mean planes of the two biuret ligand molecules in (I) is  $1.90(13)^\circ$ .

The Ni atom in (I) is slightly displaced from the least-squares plane of the approximate square of biuret O atoms ( $O1-O4$ ) coordinating to it, by  $0.0086(13) \text{ \AA}$ . The biuret  $O_4$  square itself is slightly folded, with deviations from the  $O1-O4$  mean plane of  $-0.0121(12)$ ,  $0.0119(12)$ ,  $0.0121(12)$  and


**Figure 3**

Projection on to (100) of (I), showing the hydrogen-bond cross-linking (dashed lines) between the chains shown in Fig. 2.

$-0.0119(12) \text{ \AA}$  for atoms O1, O2, O3 and O4, respectively. In the copper analogue (Freeman & Smith, 1966), the  $CuO_4$  square is constrained by space-group symmetry to be perfectly flat. Overall, the  $[Ni(C_2H_5N_3O_2)_2]^{2+}$  grouping in (I) is close to planar [r.m.s. deviation from the mean plane =  $0.030 \text{ \AA}$ ; maximum deviation =  $0.076(3) \text{ \AA}$  for N2], whereas the  $[Cu(C_2H_5N_3O_2)_2]^{2+}$  grouping in  $[Cu(C_2H_5N_3O_2)_2]Cl_2$  is distinctly puckered (Freeman & Smith, 1966) about the  $O \cdots O'$  axes (bite lines) of the biuret molecules. As well as electrostatic and van der Waals forces, numerous hydrogen bonds (Table 2) help to define the crystal packing in (I). These include  $N-H \cdots O$  bonds (mean  $H \cdots O = 2.17 \text{ \AA}$ , mean  $N-H \cdots O = 164^\circ$  and mean  $N \cdots O = 2.991 \text{ \AA}$ ) to O acceptors from both the biuret and the water ligands,  $N-H \cdots Cl$  interactions (mean  $H \cdots Cl = 2.46 \text{ \AA}$ , mean  $N-H \cdots Cl = 162^\circ$  and mean  $N \cdots Cl = 3.278 \text{ \AA}$ ) and  $O-H \cdots Cl$  interactions (mean  $H \cdots Cl = 2.19 \text{ \AA}$ , mean  $O-H \cdots Cl = 159^\circ$  and mean  $O \cdots Cl = 3.068 \text{ \AA}$ ).

Perhaps the most interesting hydrogen bonds are  $N3-H4 \cdots O3^{iii}$  and  $N4-H6 \cdots O2^{iv}$  (see Fig. 2 and Table 2 for symmetry information), which link the  $[Ni(C_2H_5N_3O_2)_2(H_2O)_2]^{2+}$  groupings into a chain propagating along [100]. The supramolecular (Bernstein *et al.*, 1995) motif is an  $R_2^2(8)$  ring. The remaining H bonds serve to crosslink the [100] chains into a three-dimensional network (Fig. 3) *via* the chloride ions. Overall, Cl1 and Cl2 accept five hydrogen bonds each.

## Experimental

Aqueous solutions of NiCl<sub>2</sub> and biuret (both 0.1 M) were mixed in a 1:1 ratio at room temperature, resulting in a green solution. Small block-like green crystals of (I) grew over the course of a few days as the water slowly evaporated and were harvested by vacuum filtration and washing with acetone.

## Crystal data

|   |   |
|---|---|
| [Ni(C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> | $D_x = 1.780 \text{ Mg m}^{-3}$           |
| $M_r = 371.82$  | Mo $K\alpha$ radiation                    |
| Monoclinic, $P2_1/c$  | Cell parameters from 3015 reflections     |
| $a = 7.3872 (4) \text{ \AA}$  | $\theta = 3.0\text{--}29.5^\circ$         |
| $b = 27.5675 (16) \text{ \AA}$  | $\mu = 1.82 \text{ mm}^{-1}$              |
| $c = 7.6687 (4) \text{ \AA}$  | $T = 293 (2) \text{ K}$                   |
| $\beta = 117.344 (1)^\circ$   | Block, green                              |
| $V = 1387.21 (13) \text{ \AA}^3$  | $0.15 \times 0.12 \times 0.10 \text{ mm}$ |
| $Z = 4$   |   |

## Data collection

|  |  |
|--|--|
| Bruker SMART 1000 CCD diffractometer                     | 4037 independent reflections           |
| $\omega$ scans   | 2416 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1999) | $R_{\text{int}} = 0.053$               |
| $T_{\text{min}} = 0.773$ , $T_{\text{max}} = 0.839$      | $\theta_{\text{max}} = 30.0^\circ$     |
| 14042 measured reflections                               | $h = -10 \rightarrow 8$                |
|  | $k = -38 \rightarrow 38$               |
|  | $l = -9 \rightarrow 10$                |

## Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | H-atom parameters constrained                        |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | $w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$              |
| $wR(F^2) = 0.101$               | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $S = 0.96$                      | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| 4037 reflections                | $\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$  |
| 172 parameters                  | $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Ni1—O3      | 2.014 (2) | Ni1—O1      | 2.024 (2) |
| Ni1—O2      | 2.018 (2) | Ni1—O6      | 2.080 (2) |
| Ni1—O4      | 2.024 (2) | Ni1—O5      | 2.083 (2) |
| O1—C1—N2—C2 | −5.1 (6)  | O4—C4—N5—C3 | 4.3 (6)   |
| O2—C2—N2—C1 | 6.7 (6)   | O3—C3—N5—C4 | −3.3 (6)  |

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D\text{---}H\cdots A$              | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|-------------------------------------|----------------|-------------|-------------|------------------------|
| N1—H1 $\cdots$ Cl2 <sup>i</sup>     | 0.86           | 2.49        | 3.340 (3)   | 173                    |
| N1—H2 $\cdots$ O5 <sup>ii</sup>     | 0.86           | 2.33        | 3.089 (4)   | 147                    |
| N2—H3 $\cdots$ Cl2 <sup>iii</sup>   | 0.86           | 2.45        | 3.266 (3)   | 158                    |
| N3—H4 $\cdots$ O3 <sup>iii</sup>    | 0.86           | 2.10        | 2.943 (4)   | 168                    |
| N3—H5 $\cdots$ Cl2 <sup>ii</sup>    | 0.86           | 2.43        | 3.239 (3)   | 158                    |
| N4—H6 $\cdots$ O2 <sup>iv</sup>     | 0.86           | 2.06        | 2.910 (4)   | 168                    |
| N4—H7 $\cdots$ Cl1 <sup>v</sup>     | 0.86           | 2.45        | 3.252 (3)   | 155                    |
| N5—H8 $\cdots$ Cl1 <sup>v</sup>     | 0.86           | 2.51        | 3.310 (3)   | 156                    |
| N6—H9 $\cdots$ Cl1 <sup>vi</sup>    | 0.86           | 2.41        | 3.259 (3)   | 169                    |
| N6—H10 $\cdots$ O6 <sup>vii</sup>   | 0.86           | 2.17        | 3.023 (3)   | 173                    |
| O5—H11 $\cdots$ Cl2                 | 0.94           | 2.16        | 3.068 (2)   | 161                    |
| O5—H12 $\cdots$ Cl1 <sup>iii</sup>  | 0.91           | 2.21        | 3.115 (2)   | 171                    |
| O6—H13 $\cdots$ Cl2 <sup>viii</sup> | 0.98           | 2.18        | 3.060 (2)   | 149                    |
| O6—H14 $\cdots$ Cl1 <sup>viii</sup> | 0.88           | 2.20        | 3.027 (2)   | 155                    |

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

The water H atoms were found in difference maps and were refined as riding on their carrier atoms in their as-found relative positions. The N-bound H atoms were placed in calculated positions assuming  $sp^2$  hybridization for the N atoms and refined as riding on their carrier atoms. The constraint  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$  was applied in all cases.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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