

Crystal Structure of Hexaaquanickel(II) Bis(dicyanamide) Bis(hexamethylenetetramine) Dihydrate

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Abstract : The reaction of tris(ethylenediamine)nickel(II) chloride with ammonia and formaldehyde yielded a green co-crystal of hexaaquanickel(II) bis(dicyanamide) dihydrate/hexamethylenetetramine (1/2), $[(\text{H}_2\text{O})_6\text{Ni}](\text{C}_2\text{N}_3)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{H}_2\text{O}$. The nickel atom is six-coordinate in a distorted octahedral geometry; the hexamethylenetetramine molecule and dicyanamide anion interact indirectly, through the coordinated water molecules, with the nickel atom. The cation, anions, hexamethylenetetramine and lattice water molecules are linked by hydrogen bonds into a tight-held coordination network structure.

Received : 19.08.02; accepted : 08.04.04

Introduction

Hydrogen-bonded assemblies belong to a subset of crystal engineering and these are usually either organic or inorganic solids [1]. Hexamethylenetetramine (hmt) is involved in both hydrogen-bonded assemblies of organic solids [2-3] and coordination polymers of various architectures [4]. The dicyanamide anion (dca), as a versatile coordination ligand (monodentate to μ_4 -coordination), forms numerous interesting metal-organic polymeric frameworks such as chains, sheets and molecular tubes [5]. This paper reports the crystal structure of a wholly hydrogen-bonded assembly of a coordination complex, hexaaquanickel(II), with both hmt and dca.

Experimental

Preparation of complex

1 g (0.03 mol) $\text{Ni}(\text{en})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in a mixture of 10 ml. water and 10 ml. aqueous formaldehyde solution (0.13 mol). Cold concentrated ammonia solution was added slowly till pH 7.3 to give a green solution. After about a month, a green gelatinous precipitate deposited on bottom of beaker and the solution became brownish. The precipitate was filtered off and evaporation of brownish solution to dryness yielded

a brown solid which was dried overnight at 90 °C in the oven; it was redissolved in water to give a green solution which on slow evaporation yielded green crystals (yield, 0.3 g) suitable for crystal structure determination.

Structure determination and refinement

Diffraction measurements on a selected crystal of dimension 0.40 x 0.20 x 0.20 mm were carried out on a Siemens P4 diffractometer. The intensities were measured at room temperature with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) to $\theta = 27.55^\circ$; 3274 reflections were measured, and these were averaged to 3089 ($R_{\text{int}} = 0.010$), of which 2969 were considered 'observed' as they satisfied the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods and refined to $R = 0.042$ ($wR = 0.133$)[6]. The water hydrogen atoms were located and refined subject to O-H and H \cdots H restraints of 0.85 ± 0.01 and $1.39 \pm 0.01 \text{ \AA}$; additionally, the Ni \cdots H interactions for each water molecule were restrained by a SADI instruction.

Crystal data: $\text{C}_{16}\text{H}_{40}\text{N}_{14}\text{NiO}_8$, $FW = 615.33$, triclinic, $P-1$, $a = 9.244(3)$, $b = 9.334(4)$, $c = 9.362(2) \text{ \AA}$, $\alpha = 76.55(2)$, $\beta = 79.55(2)$, $\gamma = 60.61(2)^\circ$, $V = 682.4(4) \text{ \AA}^3$, $\rho = 1.497 \text{ g cm}^{-3}$, $Z = 1$. CCDC No. 191555.

Table 1. Atomic coordinates and isotropic temperature factors $[(\text{H}_2\text{O})_6\text{Ni}](\text{C}_2\text{N}_3)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{H}_2\text{O}$

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni1	½	½	½	0.0258(2)
O1 _w	0.3308(2)	0.6658(2)	0.6352(2)	0.043(1)
O2 _w	0.3022(2)	0.5650(2)	0.3868(2)	0.037(1)
O3 _w	0.5370(2)	0.6905(2)	0.3769(2)	0.045(1)
O4 _w	0.2151(3)	0.7065(3)	1.1875(2)	0.054(1)
N1	0.0169(2)	0.7728(2)	0.6627(2)	0.035(1)
N2	0.2138(2)	0.6734(2)	0.6510(2)	0.035(1)
N3	0.2051(3)	0.7547(3)	0.8778(2)	0.038(1)
N4	0.3138(2)	0.9658(2)	0.6617(2)	0.039(1)
N5	0.2285(4)	0.7665(3)	1.1236(3)	0.056(1)
N6	0.3340(4)	0.7675(4)	0.8902(3)	0.063(1)
N7	0.1001(4)	1.0836(4)	0.7807(3)	0.061(1)
C1	0.0466(3)	0.6581(3)	0.6022(3)	0.036(1)
C2	0.0378(3)	0.7372(3)	0.8243(3)	0.040(1)
C3	0.1445(3)	0.9437(3)	0.6129(3)	0.038(1)
C4	0.2296(3)	0.6392(3)	0.8130(3)	0.038(1)
C5	0.3362(3)	0.8459(3)	0.6013(3)	0.039(1)
C6	0.3281(3)	0.9262(3)	0.8228(3)	0.043(1)
C7	0.3334(4)	0.7152(4)	1.0209(4)	0.059(1)
C8	0.2370(8)	0.9433(8)	0.8132(6)	0.095(1)

*U*_{eq} is defined as one-third the trace of the *U*_{ij} tensor.

Table 2 : bond distance (Å) and angles (°)

Ni1-O1 _w	2.064(2)	O1 _w -Ni1-O1 _w ⁱ	180.0
Ni1-O2 _w	2.037(2)	O1 _w -Ni1-O2 _w	86.2(1)
Ni1-O3 _w	2.027(2)	O1 _w -Ni1-O2 _w ⁱ	93.8(1)
N1-C2	1.469(3)	O1 _w -Ni1-O3 _w	87.7(1)
N1-C3	1.470(3)	O1 _w -Ni1-O3 _w ⁱ	92.3(1)
N1-C1	1.473(3)	O2 _w -Ni1-O2 _w ⁱ	180.0
N2-C5	1.464(3)	O2 _w -Ni1-O3 _w	91.4(1)
N2-C4	1.471(3)	O3 _w -Ni1-O3 _w ⁱ	180.0
N2-C1	1.475(3)	C2-N1-C3	108.3(2)
N3-C6	1.471(3)	C2-N1-C1	108.6(2)
N3-C2	1.476(3)	C3-N1-C1	107.9(2)
N3-C4	1.475(3)	C5-N2-C4	108.7(2)
N4-C6	1.464(3)	C5-N2-C1	107.7(2)
N4-C3	1.473(3)	C4-N2-C1	108.3(2)
N4-C5	1.477(3)	C6-N3-C2	107.9(2)
N5-C7	1.231(4)	C6-N3-C4	108.3(2)
N6-C7	1.208(4)	C2-N3-C4	107.9(2)
N6-C8	1.502(7)	C6-N4-C3	108.5(2)
N7-C8	1.318(7)	C6-N4-C5	108.6(2)
C3-N4-C5	107.9(2)	C7-N6-C8	128.0(3)
<i>Hydrogen bonds</i>			
O1 _w ⋯N1	2.840(3)	N1-C1-N2	111.9(2)
O1 _w ⋯N6	2.776(3)	N1-C2-N3	112.1(2)
O2 _w ⋯N2 ^a	2.828(3)	N4-C3-N1	111.7(2)
O2 _w ⋯N5 ^b	2.696(3)	N2-C4-N3	112.0(2)
O3 _w ⋯N4 ^c	2.813(3)	N2-C5-N4	111.8(2)
O3 _w ⋯O4 _w ^d	2.675(3)	N4-C6-N3	112.0(2)
O4 _w ⋯N3	2.820(3)	N6-C7-N5	131.8(4)
O4 _w ⋯O3 _w ^e	2.675(3)	N7-C8-N6	154.5(4)

Symmetry/translational codes: *i* = 1 - *x*, 1 - *y*, 1 - *z*; *a* = -*x*, 1 - *y*, 1 - *z*;
b = *x*, *y*, *z* - 1; *c* = -*x*, 2 - *y*, 1 - *z*; *d* = 1 + *x*, *y*, *z* - 1; *e* = *x* - 1, *y*, 1 + *z*.

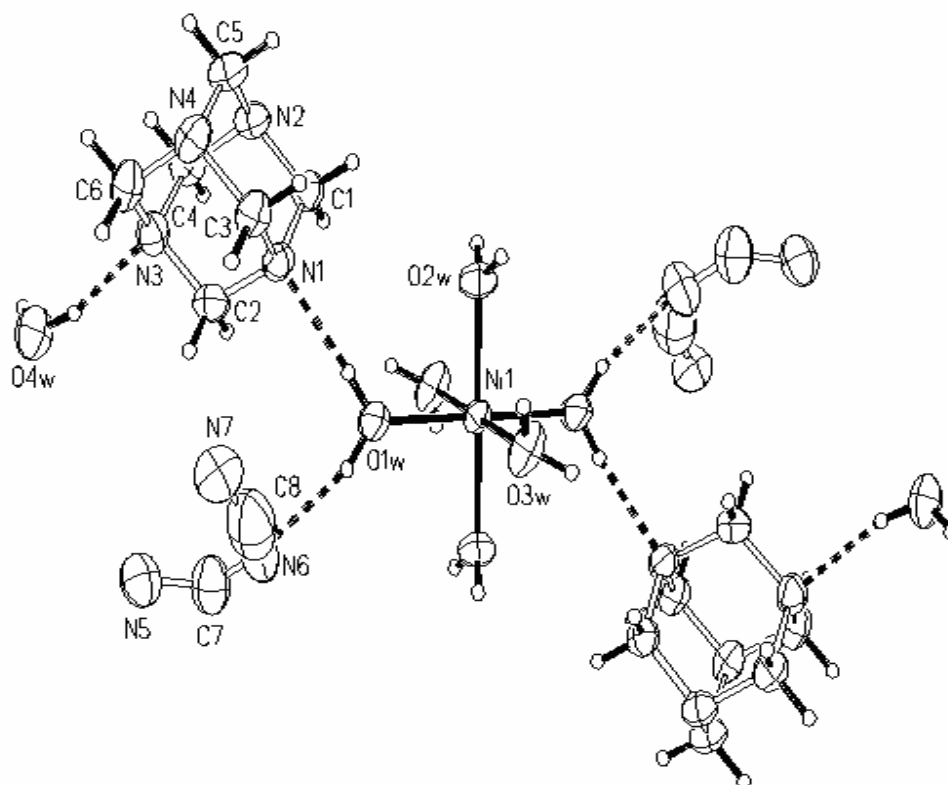


Figure 1 : ORTEP plot of $[(\text{H}_2\text{O})_6\text{Ni}](\text{C}_2\text{N}_3)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{H}_2\text{O}$ at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii; symmetry-related atoms are not labeled.

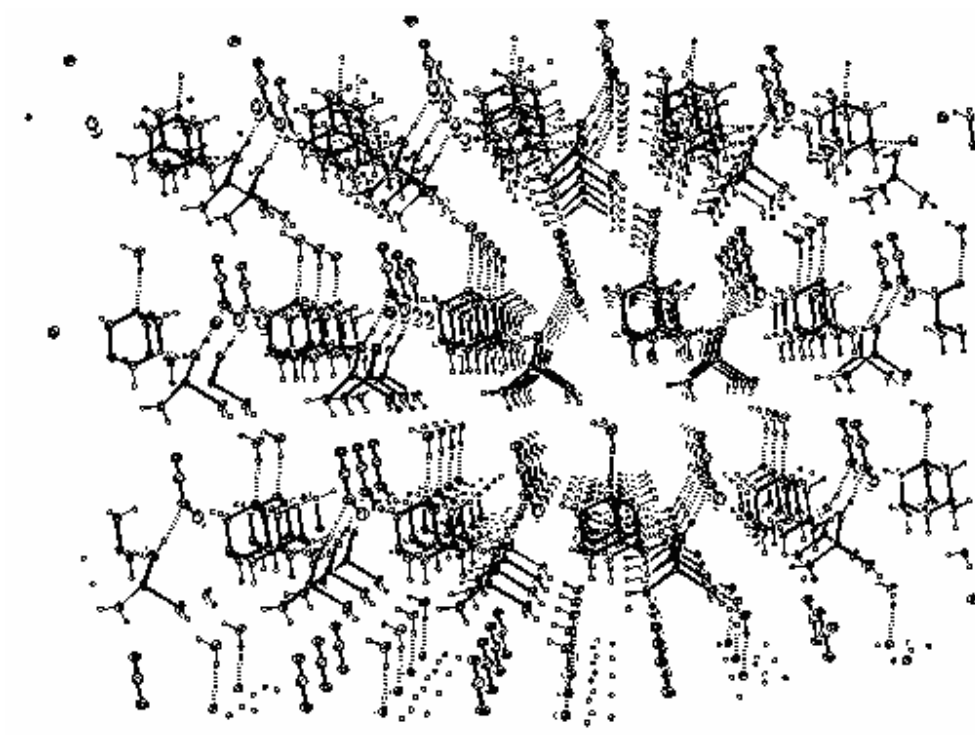


Figure 2 : Molecular aggregates with view normal to 001 plane; dotted lines show hydrogen bonding.

Discussion

The reaction mixture containing Ni(en)₃Cl₂, formaldehyde and ammonia initially yielded a green solid and a brownish substance after about a month. Both substances could not be positively identified due to their hygroscopic nature and impurities. Only the final green crystalline product, which was obtained by recrystallizing the brownish solid, was successfully characterized.

This final green compound is a hydrated co-crystal of hexaaquanickel(II) bis(dicyanamide) with a neutral organic molecule, hexamethylenetetramine. The nickel atom in the complex cation is six-coordinate, in a distorted octahedral geometry. The Ni-O (coordinated water molecule) distance averages 2.043 Å. This contrasts with the slightly more regular octahedral geometry of Ni in some simple inorganic hydrates of nickel(II) [7-8] and nickel(II) Tutton's salts [9-10]. However, such deviation from the regular octahedron seems to be more common in nickel(II) salts which contain organic anions [11-12]. The hmt and dca in the present compound is merely linked to the coordinated water molecules and the lattice water molecules, resulting in a tightly-held network structure.

The hmt molecule in the above green crystalline compound is formed from the reaction of formaldehyde and ammonia [13]. Our literature review indicates that this is a new synthesis of dca as our starting materials are Ni(en)₃Cl₂·2H₂O, formaldehyde and ammonia. However, both hmt and dca failed to coordinate to Ni in this instance.

Acknowledgement

The authors like to thank Tunku Abdul Rahman

College (01-1404), Universiti Sains Malaysia and Universiti Malaya for supporting this work.

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