Note

Structure of Hexakis(imidazole)nickel(II) Nitrate Water Solvate: $[Ni(Im)_6](NO_3)_2 \cdot 4H_2O$

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Crystal structure of the title compound, $[Ni(Im)_6](NO_3)_2 \cdot 4H_2O$ (Im = imidazole), was determined by X-ray crystallographic analysis. The crystal structure consists of discrete $Ni(Im)_6^{2+}$ cation, NO_3^- anion and four uncoordinated water molecules. It crystallizes in the hexagonal system, space group *P*63, with lattice parameters $a = b = 0.9003(2)$ nm, $c = 2.1034(4)$ nm, and $Z = 2$. The Ni(II) ion is centro- symmetric octahedron geometry with the NiN_6 core. Six imidazole molecules are coordinated to each nickel(II) atom through its tertiary nitrogen atom. The short and long bond distances of Ni—N are 0.2059(6) and 0.2204(7) nm, respectively. In the solid state, $[Ni(Im)_6]^{2+}$, H_2O moieties and nitrate anions form the three dimensional hydrogen bonds network which stabitizes the crystal structure.

Keywords nickel complex, imidazole ligand, octahedron geometry, hydrogen bond network

Introduction

Imidazole has attracted considerable interest as a ligand in many biological systems in which it provides a potential binding site for metal ions.[1] Imidazole itself is an unidentate ligand and forms complexes with metal ions through its tertiary nitrogen atom. Some complexes of imidazole and its derivatives with transition-metal ions have been reported.[2,3] The coordination number of the low-spin square-planar nickel(II) complexes is often increased by the addition of the other ligands to form high-spin octahedral nickel(II) complexes with donor ligands containing nitrogen.[4,5] Recently, metal complexes with ligands containing nitrogen as donors received much attention due to their wide use in nonlinear optical materials.[6,7] To the best of our knowledge, strong (O—H···O and N—H···O hydrogen bonds), weak (van der Waals, $\pi \cdots \pi$ stacking) and potentially weak (C—H···Y hydrogen bonds, Y = O and N) intermolecular interactions generally play an important role in the process of molecular recognition and self-assembly of molecules.[8] In previous work, we reported some imidazole metal complexes with strong hydrogen bond network.[9,10] In this paper, the crystal structure of hexakis(imidazole)nickel(II) nitrate water solvate, $[Ni(Im)_6]NO_3 \cdot 4H_2O$ was described.

Experimental

Elemental analysis was performed using a PE-240C elemental analyzer. All chemicals were of analytical grade and used directly without further purification.

To a warm solution of imidazole (1.0 g, 15 mmol) in EtOH (50 mL) was added $Ni(NO_3)_2$ (0.46 g, 2.5 mmol) with stirring and refluxed for 2 h. The solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a deep green crystalline solid appeared several weeks later and was separated by filtration. The C, H and N content was deter-

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mined by elemental analysis (Anal. calcd for $C_{18}H_{38}N_{14}NiO_{10}$: C 32.30, H 5.72, N 29.30%; found C 31.96, H 5.95, N 29.04).

A summary of the key crystallographic information is given in Table 1. The selected crystal of $[Ni(Im)_6](NO_3)_2 \cdot 4H_2O$ was mounted on an Rigaku Raxis-IV diffractometer. Reflection data were measured at 293 K, using graphite monochromated Mo Kα (λ = 0.071073 nm) radiation ω-2θ scan mode. Intensities were corrected for Lorentz and polarization effects, empirical absorption, and the data reduction using SADABS[11] program.

The structure was solved by direct methods using SHELXS-97.[12] All the non-hydrogen atoms were refined on F^2 anistropically by full-matrix least squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0726$, $R_w = 0.1130$ for 2181 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.2230P)^2 + 5.9000P]$, where $P = (F_o^2) + 2(F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.[13] The final position parameters of non-hydrogen atoms are given in Table 2.

Results and discussion

The structure of the title compound consists of discrete $Ni(Im)_6^{2+}$ cation, NO_3^- anion and four uncoordinated water molecules. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 2 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths, angles and hydrogen bond distances are presented in Tables 3 and 4.

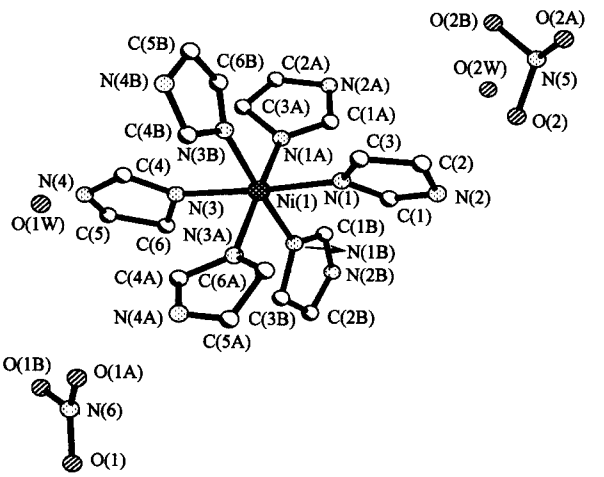

Fig. 1 Molecular structure of $[Ni(Im)_6](NO_3)_2 \cdot 4H_2O$ with the atomic numbering scheme.

Table 1 Summary of crystallographic results for the title compound

Empirical formula	$C_{18}H_{38}N_{14}NiO_{10}$
Formula weight	669.28
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	hexagonal, $P63$
Unit cell dimensions	$a = 0.90035(13)$ nm; $b = 0.90035(13)$ nm; $c = 2.1034(4)$ nm
Volume	1.4766(4) nm^3
Z, calculated density	2, 1.307 Mg/m^3
Absorption coefficient	0.697 mm^{-1}
$F(000)$	608
Crystal size	0.3 mm × 0.3 mm × 0.2 mm
θ range for data collection	1.94°—27.57°
Limiting indices	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 5$, $-27 \leqslant l \leqslant 27$
Reflections collected/unique	5364/2181 [$R_{int} = 0.0475$]
Completeness to $\theta = 27.57$	98.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2181/5/126
Goodness-of-fit on F^2	1.174
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0726$, $wR_2 = 0.1130$
R indices (all data)	$R_1 = 0.0904$, $wR_2 = 0.1326$
Largest diff. peak and hole	1204 and −910 e·nm^{-3}

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^5$ nm^2) for the title compound

	x	y	z	U_{eq}[a]
Ni(1)	0	0	1272(1)	35(1)
N(6)	6667(7)	3333(7)	3738(7)	38(2)
O(2W)	-2786(11)	638(13)	-1275(8)	145(4)
O(1W)	0	0	3794(15)	69(3)
N(1)	-66(6)	1805(6)	690(3)	30(1)
C(1)	640(19)	2257(11)	139(5)	262(7)
N(2)	585(10)	3621(15)	-76(4)	86(4)
C(2)	-374(12)	4042(15)	347(4)	68(2)
C(3)	-690(11)	3061(9)	863(5)	60(2)
N(3)	-92(9)	-2076(7)	1857(3)	41(2)
C(4)	-876(8)	-2669(8)	2434(4)	34(2)
N(4)	-395(15)	-3735(10)	2687(4)	101(3)
C(5)	310(30)	-4011(16)	2309(8)	302(9)
C(6)	902(14)	-2599(11)	1811(5)	61(3)
O(1)	8301(7)	4378(8)	3805(4)	69(2)
N(5)	-3333(10)	3333(10)	-984(10)	77(6)
O(2)	-1620(80)	3150(110)	-570(40)	880(70)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths ($\times 10$ nm) and bond angles (°) of the title compound

Ni(1)—N(1)	2.059(6)	Ni(1)—N(3)	2.204(7)
N(6)—O(1)[a]	1.298(6)	N(6)—O(1)	1.298(6)
N(6)—O(1)[b]	1.298(6)	N(1)—C(1)	1.285(13)
N(1)—C(3)	1.538(11)	C(1)—N(2)	1.333(17)
N(2)—C(2)	1.417(16)	C(2)—C(3)	1.336(14)
N(3)—C(6)	1.205(15)	N(3)—C(4)	1.371(10)
C(4)—N(4)	1.345(12)	C(5)—C(6)	1.524(16)
N(5)—O(2)	1.84(7)		
N(1)[c]-Ni(1)-N(1)	88.2(2)	N(1)-Ni(1)-N(3)[c]	92.3(2)
N(3)[c]-Ni(1)-N(3)[d]	91.9(3)	N(1)[c]-Ni(1)-N(3)	87.6(2)
N(1)-Ni(1)-N(3)	175.8(2)	O(1)[a]-N(6)-O(1)	118.8(3)
O(2)-N(5)-O(2)[e]	100(3)	C(1)-N(1)-C(3)	106.6(8)

Symmetry transformations used to generate equivalent atoms: [a] $-x+y+1, -x+1, z$; [b] $-y+1, x-y, z$; [c] $-y, x-y, z$; [d] $-x+y, -x, z$; [e] $-x+y-1, -x, z$.

Table 4 Hydrogen bond distances (10 nm) of the title compound

D	H	A	Symmetry	D···A
N(2)	H(2A)	O(1)	$-x, -y, -1/2+z$	2.7982
N(2)	H(2A)	O(2)	$-x, -y, -1/2+z$	2.5179
O(2W)	H(2WA)	O(1)	$1-y, x-y, z$	2.6486
O(2W)	H(2WB)	O(2)	$-x+y, 1-x, z$	2.4842
O(2W)	H(2WA)	O(2)	$1-y, x-y, z$	2.4842
O(2W)	H(2WA)	N(5)	$-x+y, 1-x, z$	2.7798
O(2W)	H(2W)	O(1W)	$-y, x-y, z$	2.8383
O(1W)	H(1W)	O(2W)	$-x+y, 1-x, z$	2.6486

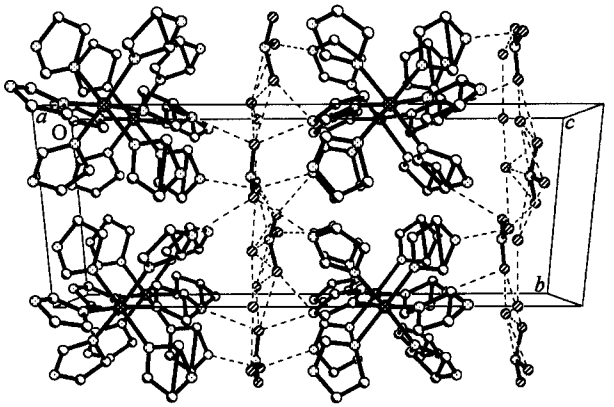

Fig. 2 Packing diagram of the unit cell of $[Ni(Im)_6]NO_3 \cdot 4H_2O$ showing the hydrogen bond network.

The Ni(II) ion assumes a centro-symmetric octahedron geometry. The polyhedron about nickel can be described as octahedron with six nitrogen atoms from six neutral imidazole ligands. Six imidazole molecules through the tertiary nitrogen atoms are coordinated to each Ni(II) ion, and two nitrate anions in general position balance the charges. The bond distances of Ni—N are fashion with a short bond Ni(1)—N(1) [0.2059(6) nm] and a long bond Ni(1)—N(3) [0.2204(7) nm], which are slightly different with those observed in the similar structures, $[Ni(Im)_6(NO_3)(OH)(H_2O)_4]$[14] [0.2124 (5) nm], $[Ni(Im)_6(NO_3)_2]$[15] [0.2128(2) nm] and $[Ni(Im)_6](Sal)_2$[16] [0.2120(1), 0.2124(1) and 0.2141(1) nm].

The crystal packing is stabilized by extensive hydrogen bonding. The $Ni(Im)_6^{2+}$ is connected with the free NO_3^- anion by hydrogen bonding (Fig. 2) [the donor and acceptor distances are N(2)···O(1) 0.27982(3) nm (symmetry code: $-x$, $-y$, $-1/2+z$); N(2)···O(2) 0.25179(3) nm (symmetry code: $-x$, $-y$, $-1/2+z$)], while the NO_3^- anion is hydrogen bonded to the uncoordinated water molecules (O(1)···O(2W) 0.26486 (3) nm, O(2)···O(2W) 0.24842(4) nm (symmetry code: $1-y$, $1+x-y$, z and $-x+y$, $1-x$, z), N (5)···O(2W) 0.27798(3) nm (symmetry code: $-x+y$, $1-x$, z)], and these water molecules connect with the other water molecule [O(2W)···O(1W) 0.28383(4) nm (symmetry code: $-y$, $x-y$, z and $-x+y$, $-x$, z), the O(2W)···O(1W) distance is similar to that of pure water (0.283 nm)].[17] All above hydrogen bonds in this structure connect $[Ni(Im)_6]^{2+}$, H_2O moieties and nitrate anions forming the three dimensional hydrogen bonds network which stabilizes the crystal structure.

References

1 Brooks, P.; Davidson, N. *J. Am. Chem. Soc.* **1960**, *82*, 2118.

2 Eilbeck, W. J.; Holmes, F.; Underhill, A. E. *J. Chem. Soc. A* **1967**, 757.

3 Davis, W. J.; Smith, J. *J. Chem. Soc. A* **1971**, 317.

4 Coucouvanis, D. *Prog. Inorg. Chem.* **1977**, *26*, 301.

5 Cusumane, M. *Inorg. Chem.* **1979**, *35*, 65.

6 Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z.; Huang, X. Y. *J. Coord. Chem.* **1996**, *38*, 219.

7 Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z.; Fun, H. K.; Sivakumar, K. *Polyhedron* **1996**, *15*, 2263.

8 Jian, F. F.; Wang, Z. X.; Bai, Z. P.; You, X. Z.; Chen, W. *Transition Met. Chem.* **1999**, *24*, 589.

9 Wang, Z. X.; Jian, F. F.; Zhang, Y. R.; Li, F. S.; Fun, H. K.; Chinnakali, K. *J. Chem. Crystallogr.* **1999**, *29*, 885.

10 Sheldrick, G. M. *SHELXTL5*, The complete software package for single crystal structure determination, Siemens, AG, Analytical Systems Aut37, D76181 Karlsruhe 21, Germany, **1995**.

11 Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1969**, *46*, 467.

12 Sheldrick, G. M. *SHELXTL93*, Program for crystal structure refinement, University of Gottingen, Germany, **1993**.

13 Wilson, A. J. *International Table for X-Ray Crystallography*, Volume C, Kluwer Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500—502) and 4.2.6.8 (pp. 219—222) respectively.

14 Niu S. Y.; Yang Z. Z.; Yang, Q. C.; Hou, Y. Y.; Yang, G. D.; Bu, W. M. *Chem. J. Chin. Univ.* **1999**, *11*, 1671 (in Chinese).

15 Finney, A. J.; Hitchman, M. A.; Raston, C. L.; Rowbottom, G. L.; White, A. H. *Aust. J. Chem.* **1981**, *34*, 2113.

16 Jian, F. F.; Wang, Z. X.; Bai, Z. P.; You, X. Z.; Fun, H. K.; Chinnakali, K. *J. Chem. Crystallogr.* **1999**, *29*, 359.

17 Jian, F. F.; Lin, J. H.; Zhang, S. S. *Chin. J. Chem.* **2001**, *19*, 772.

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