J Chem Crystallogr (2008) 38:529–532
DOI 10.1007/s10870-008-9368-0

ORIGINAL PAPER

Synthesis and Crystal Structure of Nickel(II) Complex with 2,2′-Biimidazole and 4-Aminobenzoic Acid

Yanping Li · Pin Yang

Received: 9 May 2007 / Accepted: 27 March 2008 / Published online: 11 April 2008

Abstract The Ni(II) complex, $[Ni(H_2biim)_2(PABA)_2]Cl_2 \cdot 2H_2O$, H_2biim being 2,2′-biimidazole, PABA being 4-aminobenzoic acid has been synthesized and the crystal structure determined using X-ray crystallography. The complex crystallizes in triclinic system, space group $P-1$ with unit cell parameters $a = 8.3920(9)$ Å, $b = 9.8436(11)$ Å, $c = 9.8874(11)$ Å, $\alpha = 94.862(2)°$, $\beta = 109.142(2)°$, $\gamma = 90.992(2)°$, $V = 767.95(15)$ Å^3 and $Z = 1$. The molecules of the complex in the crystal assemble by way of N–H···Cl, O–H···Cl, O–H···O hydrogen bonds as well as π–π stacking interactions to provide a two-dimensional supramolecular structure.

Keywords Ni^{II} complex · Biimidazole · 4-Aminobenzoic acid · Crystal structure · Hydrogen bonding

Introduction

Hybrid inorganic–organic materials have received much attention because they incorporate the functionality of both components [1, 2]. Studies related to the design and crystal supramolecularity of these materials are regarded as being within the inorganic crystal engineering field [3], which has allowed the development and exploitation of rational strategies leading to metal-containing extended supramolecular entities [1, 2]. These strategies have been focused on the assembly of organic/metal moieties capable of driving self-recognition or self-assembly, mainly by complementary hydrogen bonds [1–4] and/or coordination bonds [5]. In fact, the consideration and utilization of both supramolecular interactions has generated a great diversity of metal-based architectures in the solid state [6]. Herein, we are concerned with the family of hybrid materials in which a metal centre provides the orientation ability of its well-known coordination environment, to form inorganic hydrogen-bonded assemblies. It is frequently argued that these hydrogen-bonded networks are less robust than stronger bonds of inorganic analogues. However, the number and/or the strength of a particular hydrogen bond may act in concert, in principle, in an assembly robust enough to withstand, for instance, guest removal [7]. Recently, Beatty [8] has reported an extensive revision on the crystal engineering of extended systems based on hydrogen bonded coordination complexes.

A particular organic target for construction of hybrid materials is the neutral molecule 2,2′-biimidazole (H_2biim) and its monoanionic derivative ($Hbiim^-$). Both molecular moieties possess a double property, namely they can be coordinated to metal centres and can act as a donor in hydrogen bonding interactions [9]. In the present study we describe the synthesis, structure and characterization of a new supramolecular complex $[Ni(H_2biim)_2(PABA)_2]Cl_2 \cdot 2H_2O$.

Experimental

Synthesis of $[Ni(H_2biim)_2(PABA)_2]Cl_2 \cdot 2H_2O$

The 2,2′-biimidazole (H_2biim) ligand was synthesized according to the method reported in the literature [10]. To a solution of $NiCl_2 \cdot 6H_2O$ (0.30 mmol) in 50 mL of hot

Y. Li · P. Yang (✉)
Institute of Molecular Science, Chemical Biology and Molecular Engineering, Laboratory of Education Ministry, Shanxi University, Taiyuan 030006, P.R. China
e-mail: yangpin@sxu.edu.cn

water, 0.60 mmol of H_2biim was added. To the resulting mixture, a solution of 4-aminobenzoic acid (PABA, 0.60 mmol) previously dissolved in 30 mL of hot water was added. The solution was then concentrated to one-third of its initial volume. The resulting solution was allowed to evaporate slowly at room temperature. After two months, blue single crystals of the complex appeared. Yield: 75%.

Anal. Calcd for $C_{26}H_{30}Cl_2N_{10}O_6Ni$: C, 44.07; H, 4.24; N, 19.77%; found C, 44.15; H 4.21; N, 19.84%.

Crystal Structure Determination and Refinement

A blue block crystal of the complex was mounted on a glass fiber and used for data collection. Cell dimensions and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 3197 reflections with $2.57 < \theta < 27.02$ using a Bruker SMART APEX CCD automatic diffractometer. Reflection data were collected at 298 K using Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the program SAINT [11] and empirical absorption correction was carried out using SADABS 12] program.

The structure was solved by direct methods (SHELXS97), refinement was done by full-matrix least-squares on F^2 using the SHELXL97 program suite [13]. In final cycles, all nonhydrogen positions were refined by anisotropic temperature factors. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding on their respective nonhydrogen atoms. The hydrogen atoms of the water molecule were located from the difference Fourier and included as such in the refinement and were riding on water oxygen. A summary of the crystal data, experimental details, and refinement results is given in Table 1. Crystallographic data for the structure reported in this paper have also been deposited with the Cambridge Crystallographic Data Center (No. 628782).

Table 1 Crystal data for $[Ni(H_2biim)_2(PABA)_2]Cl_2{\cdot}2H_2O$

Deposition numbers	CCDC 628782
Empirical formula	$C_{26}H_{30}Cl_2N_{10}O_6Ni$
Color/shape	Blue/block
Formula weight	708.21
Temperature (K)	298(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P − 1
Unit cell dimensions	8.3920(9)
a (Å)	9.8436(11)
b (Å)	9.8874(11)
c (Å)	94.862(2)
α (°)	109.142(2)
β (°)	90.992(2)
γ (°)	767.95(15)
V (Å^3)	1
Z	1.531
D_{calc} (g cm^{-3})	0.30 × 0.30 × 0.20
Crystal size (mm)	366
F(000)	3790
Reflections collected	2653
Unique reflections	2.08–25.01
θ Range for data collection (°)	$-9 \le h \le 8$
Index ranges	$-11 \le k \le 11$
Absorption coefficient (mm^{-1})	$-7 \le l \le 11$
Data/restrains/parameters	0.864
Final R indices [$I > 2\sigma$ (I)]	2653/0/206
R indices (all data)	R1 = 0.0304, wR2 = 0.0751
Goodness-of-fit	R1 = 0.0308, wR2 = 0.0753
Largest difference in peak and hole (e Å^{-3})	1.069 0.274 and −0.283

Result and Discussion

The structure of the complex is depicted in Fig. 1. Significant bond parameters are given in Table 2.

The asymmetric unit contains one half of $[Ni(H_2biim)_2(PABA)_2]^{2+}$ cation with the nickel ion located on an

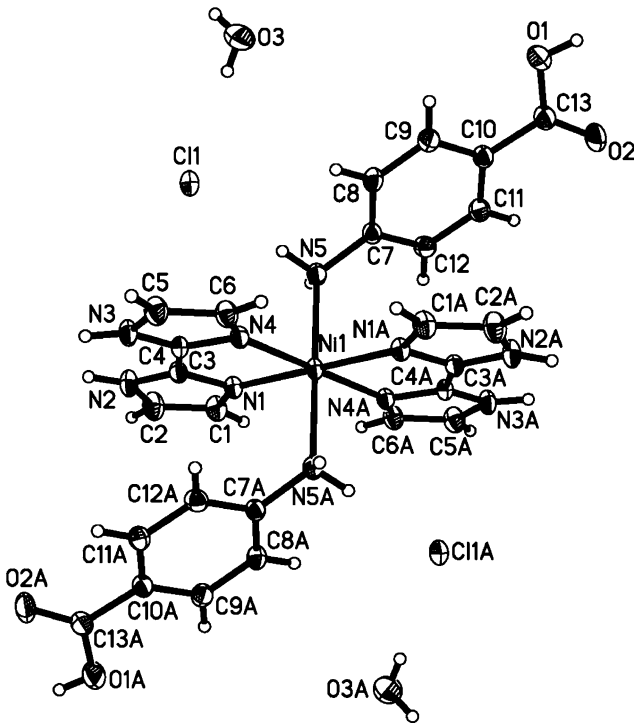

Fig. 1 Molecular structure of $[Ni(H_2biim)_2(PABA)_2]Cl_2{\cdot}2H_2O$, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms

Table 2 Selected bond lengths (Å) and angle (°) for $[Ni(H_2biim)_2(PABA)_2]Cl_2 \cdot 2H_2O$

Bond	*d* (Å)	Bond	*d* (Å)	Angle	ω (°)
Ni(1)–N(1)	2.0828(15)	C(6)–C(5)	1.355(3)	N(5)–Ni(1)–N(5A)	180
Ni(1)–N(4)	2.0966(16)	C(5)–N(3)	1.364(3)	N(1)–Ni(1)–N(1A)	180.00(9)
Ni(1)–N(5)	2.2102(16)	N(3)–C(4)	1.338(3)	N(4)–Ni(1)–N(4A)	180
C(13)–O(1)	1.317(3)	C(4)–C(3)	1.442(3)	N(1)–Ni(1)–N(4)	80.37(6)
C(13)–O(2)	1.208(3)	C(3)–N(2)	1.334(3)	N(1)–Ni(1)–N(5)	85.97(6)
N(4)–C(6)	1.369(3)	N(2)–C(2)	1.364(3)	N(4)–Ni(1)–N(5)	92.15(6)

Symmetry codes: (A) -x, -y, -z+2

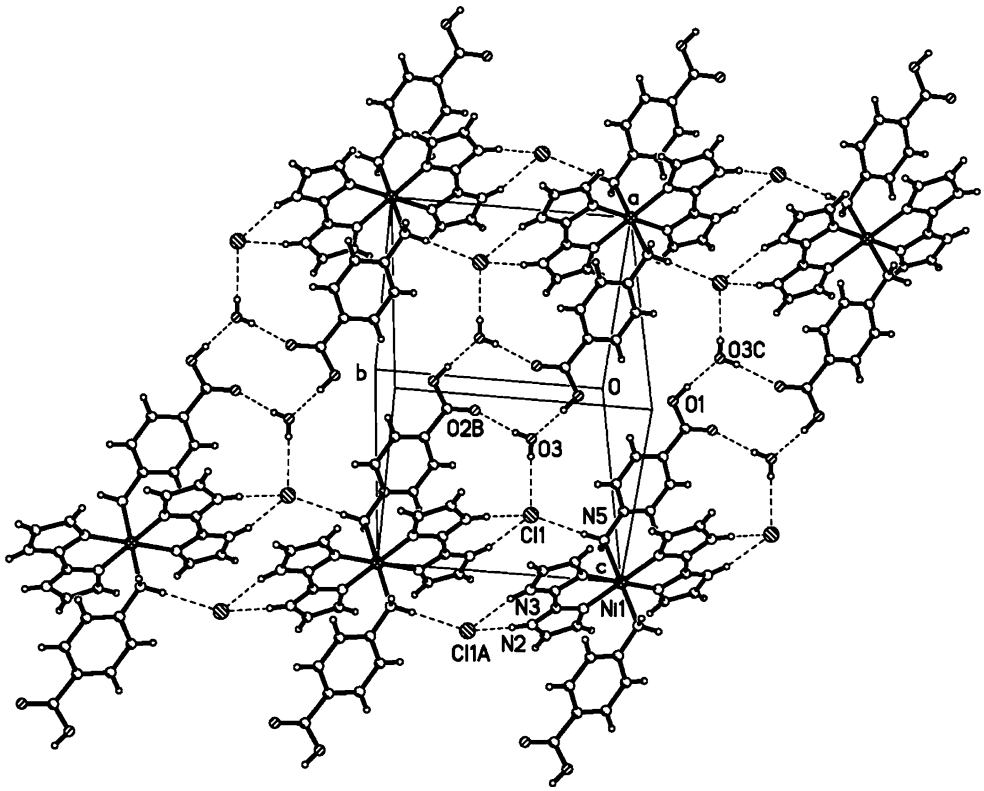

Fig. 2 Hydrogen-bonded 2D-network (hydrogen bonds are shown as dashed lines)

inversion centre, one Cl^- anion and one water molecule of crystallisation. In the complex cation $[Ni(H_2biim)_2(PABA)_2]^{2+}$, the central metal atom nickel allows the formation of a distorted octahedral coordination environment with four nitrogen atoms of two H_2biim ligands arranged *trans* to each other. Two nitrogen atoms of two PABA, axial to the metal-biimidazole plane, occupy the remaining coordination sites. The N(1)–Ni(1)–N(4) bite angle generated by the chelating of the biimidazole is 80.37(6)°, which lies in the range [78.7°–80.9°] [14] registered in the CSD so far. The Ni–N(H_2biim) lengths and the average angles and distances in the biimidazole ligands also are comparable with those previously reported in the CSD [14]. The Ni–N(PABA) length is 2.2102(16) Å, also comparable with that reported previously [15]. The two imidazole rings are almost coplanar with the dihedral angle of 5.5°.

Figure 2 shows the 2D hydrogen-bonded network of the title complex wherein neighbouring cations, anions and water molecules are interconnected by the two kinds of synthons R_2^1 (7) and R_4^4 (12) as well as O–H···Cl hydrogen bonds (Table 3). The R_2^1 (7) ring is formed by the hydrogen bonds between Cl^- and H_2biim, which is similar to that reported before [16]. The R_4^4 (12) ring is formed by the hydrogen bonds between PABA and water molecules. The network is further stabilized by π–π interactions among benzene rings with the face-to-face distance of 3.503 Å.

Table 3 Hydrogen bonding parameters for $[Ni(H_2biim)_2(PABA)_2]Cl_2 \cdot 2H_2O$

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	D–Ĥ···A (°)
N(3)–H(4)···Cl(1A)	3.2019(18)	0.86	2.4	155.2
N(5)–H(8)···Cl(1)	3.3628(18)	0.9	2.46	176.4
N(2)–H(3)···Cl(1A)	3.1080(19)	0.86	2.3	157.7
O(3)–H(15)···Cl(1)	3.0995(19)	0.72	2.38	176.3
O(3)–H(14)···O(2B)	2.789(3)	0.76	2.03	171.7
O(1)–H(13)···O(3C)	2.603(3)	0.82	1.79	172.5

Symmetry codes: (A) −x, −y+1, −z+2; (B) x, y+1, z; (C) −x+1, −y, −z

Acknowledgments We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (No.30470408) and the Shanxi Provincial Natural Science Foundation for Youth (No. 20041032).

References

1. Aakeröy CB, Beatty AM, Lorimer KR (2000) J Chem Soc Dalton Trans 3869
2. Gillon AM, Lewis GR, Orpen AG, Rotter S, Starbuck J, Wang X, Rodríguez-Martín Y, Ruiz-Pérez C (2000) J Chem Soc Dalton Trans 3897
3. Braga, DJ (2000) Chem Soc Dalton Trans 1
4. (a) Brammer L (2003) Dalton Trans 3145 (b) Brammer, L, Mareque Rivas JC, Atencio R, Fang S, Pigge FC (2000) J Chem Soc Dalton Trans 3855 (c) Mareque Rivas JC, Brammer L (1999) Coord Chem Rev 183:43
5. (a) Blake AJ, Champness NR, Cooke PA, Nicolson JEB (2000) Chem Commun 665 (b) Blake AJ, Champness NR, Hubberstey P, Li WS, Withersby MA, Schröder M (1999) Coord Chem Rev 183:117 (c) Batten SR, Hoskins BF, Robson R (2000) Chem Eur J 6:156
6. Zaworotko MJ (2001) Chem Commun 1
7. (a) Kepert CJ, Hesek D, Beer PD, Rosseinsky MJ (1998) Angew Chem Int Ed 37:3158 (b) Te RL, Griesser UJ, Morris KR, Byrn SR, Stowell JG (2003) Cryst Growth Des 3:997
8. Beatty AM (2001) Cryst Eng Commun 3:243
9. (a) Fortin S, Beauchamp AL (2001) Inorg Chem 40:105 (b) Sang R, Zhu M, Yang, P (2002) Acta Crystallogr Sect E 58:172 (c) Drew MGB, Félix V, Gonçalves IS, Kühn, FE, Lopes AD, Romao CC (1998) Polyhedron 17:1091 (d) Fortin S, Fabre P-L, Dartiguenave M, Beauchamp AL (2001) J Chem Soc Dalton Trans 3520 (e) Bélanger S, Beauchamp AL (1999) Acta Crystallogr Sect C 55:517 (f) Avilés T, Dinis A, Calhorda MJ, Pinto P, Félix V, Drew MGB (2001) J Organomet Chem 625:186 (g) Cancela J, Gonzáles-Garmendia MJ, Quirós M (2001) Inorg Chim Acta 313:156
10. Melloni P, Dradi E, Longemann W (1972) J Med Chem 15:926
11. Sheldrick GM (1996) SAINT v4 software reference manual. Siemens Analytical X-ray Systems, Madison, WI
12. Sheldrick GM (1996) SADABS, program for empirical absorption correction of area detector data. University of Göttingen, Germany
13. Sheldrick GM (1997) SHELXS97, SHELXL97, program for crystal structure analysis. University of Göttingen, Germany
14. Allen FH (2002) The Cambridge structural database. Acta Cryst Sect B 58:380
15. Liu BX, Xu DJ (2006) Acta Cryst Sect E 62:2670
16. Li YP, Yang P (2006) Acta Cryst Sect E 62:o3223