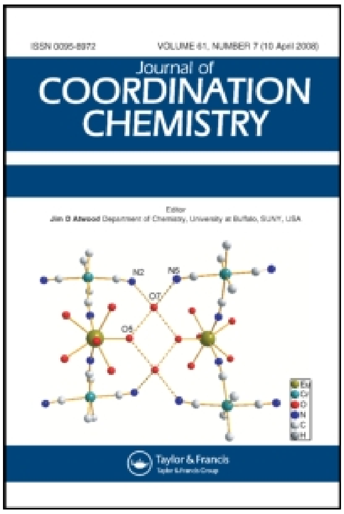

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Synthesis and crystal structure of aqua(diaminobithiazole)(iminodiacetato)nickel(II) hydrate

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Synthesis and crystal structure of aqua(diaminobithiazole)(iminodiacetato)nickel(II) hydrate

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Crystals of the title compound, $[(C_6H_6N_4S_2)(C_4H_5NO_4)(H_2O)Ni]\cdot H_2O$, consist of the Ni(II) complex and lattice water. The Ni(II) complex adopts a distorted octahedral coordination geometry formed by an iminodiacetate anion (IDA), a diaminobithiazole (DABT) and a coordinated water molecule. A twisted configuration of DABT is the distinguishing feature in the complex, the dihedral angle between thiazole rings of DABT being 20.04(8)°. An aromatic stacking interaction occurs between thiazole rings from neighboring complex molecules, and is considered as the reason for the twisted configuration. The tridentate IDA dianion chelates to a Ni(II) atom in a *facial* configuration. A hydrogen bond network holds the complex molecules together to form a supramolecular structure.

Keywords: Ni(II) complex; Crystal structure; Diaminobithiazole; Iminodiacetate; Aromatic stacking

1. Introduction

Transition metal complexes with 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT) have been found to be effective inhibitors of DNA synthesis in tumor cells [1, 2]. Recently, multinuclear metal complexes with DABT Schiff bases have shown possible application in the field of soft magnetic materials [3]. A series of metal complexes with DABT has been prepared in our laboratory and crystal structures have been determined in order to understand the relationship between properties and structure. As a part of this investigation, the structure of the title complex of Ni(II) is presented below.

2. Experimental

2.1. *Preparation*

DABT was obtained in the manner reported by Erlenmeyer [4]. An aqueous solution ($20\,cm^3$) of DABT (0.2 g, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) was mixed with

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an aqueous solution (10 cm^3) containing iminodiacetic acid (H_2IDA) (0.13 g, 1 mmol) and Na_2CO_3 (0.11 g, 1 mmol). The mixture was refluxed for 2 h and filtered. Green, single crystals were obtained from the filtrate after one week. C, H and N contents were analyzed on a Carlo-Erba 1160 instrument. *Anal.* Calc. for $[(C_6H_6N_4S_2)(C_4H_5NO_4)(H_2O)Ni]\cdot H_2O$%: C, 28.29; N, 16.51; H, 3.54 Found: C, 29.40; N, 16.29; H, 3.74.

2.2. *Crystal structure determination*

X-Ray diffraction data were collected on a Rigaku RAXIS-RAPID diffractometer up to $2\theta_{max}$ of 55.0° with Mo Kα radiation at room temperature. Usual *Lp* and empirical absorption corrections [5] were applied. The crystal structure was solved by direct methods [6] followed by Fourier syntheses. Structure refinement was performed by full matrix least-squares procedures on F^2 using SHELX-97 [7]. H atoms on carbon and nitrogen atoms were placed in calculated positions and were included in the final cycles of refinement in riding mode. H atoms on oxygen atoms were located in a difference Fourier map and included in structure factor calculations with fixed positions and an isotropic thermal parameter of 0.05 Å^2.

2.2.1. Crystal data. $C_{10}H_{15}N_5NiO_6S_2$, $M = 424.10$, monoclinic, $P2_1/c$, $a = 8.07740(10)$, $b = 9.4282(3)$, $c = 21.3473(5)$ Å, $\beta = 89.480(5)°$, $V = 1625.64(7)$ Å^3, $Z = 4$, $D_x = 1.733\ \mathrm{g\,cm^{-3}}$, μ(Mo Kα) $= 1.489\ \mathrm{mm^{-1}}$, $F(000) = 872$, $S = 1.148$, $R_1 = 0.025$ and $wR_2 = 0.066$ for 087 observed reflections $[I > 2\sigma(I)]$, $R_1 = 0.030$ and $wR_2 = 0.078$ for 3462 independent reflections, $(\Delta\rho)_{max} = 0.23$ and $(\Delta\rho)_{min} = -0.34\ \mathrm{e\,Å^{-3}}$.

3. Results and discussion

Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 1. Selected bond distances and angles are listed in table 2.† The molecular structure is illustrated in figure 1. The Ni(II) complex assumes a distorted octahedral coordination geometry, formed by an IDA, a DABT and a coordinated water molecule.

A twisted configuration of DABT is the distinguishing feature in the complex, the dihedral angle between thiazole rings being 20.04(8)°; DABT is structurally similar to 2,2′-bipyridine and usually plays the role of a chelating ligand. The average C–C bond distance between thiazole rings of DABT is 1.458 Å in reported structures, ranging from 1.444 to 1.468 Å (table 3). Although this suggests a C–C single bond binding two trigonal carbon atoms, thiazole rings of DABT usually have a coplanar configuration in complexes. A comparison of the geometric parameters of DABT is listed in table 3. The dihedral angle found in the present Ni(II) complex is much different from

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†Full crystallographic data have been deposited in the CCDC with deposition number CCDC 232652.

Table 1. Atomic coordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[\times 10^3]$ for the complex.

Atom	x/a	y/b	z/c	Ueq (Å^2)
Ni	6280(1)	1789(1)	1130(1)	23(1)
S(1)	9047(1)	5804(1)	1757(1)	45(1)
S(2)	2175(1)	4649(1)	348(1)	42(1)
O(1)	7691(2)	499(2)	1718(1)	31(1)
O(2)	7295(2)	−1081(2)	2478(1)	44(1)
O(1W)	9505(2)	−927(2)	837(1)	47(1)
O(3)	5178(2)	−8(2)	795(1)	29(1)
O(4)	2838(2)	−1240(2)	837(1)	34(1)
O(5)	8056(2)	1639(2)	420(1)	35(1)
N(1)	7285(2)	3668(2)	1435(1)	28(1)
N(2)	9681(3)	3042(2)	1982(1)	56(1)
N(3)	4753(2)	3236(2)	660(1)	27(1)
N(4)	2869(2)	1935(2)	54(1)	37(1)
N(5)	4481(2)	1486(2)	1847(1)	26(1)
C(1)	8667(2)	3992(2)	1727(1)	34(1)
C(2)	7238(3)	6113(2)	1354(1)	38(1)
C(3)	6481(2)	4877(2)	1225(1)	29(1)
C(4)	4943(2)	4605(2)	889(1)	29(1)
C(5)	3676(3)	5497(2)	776(1)	40(1)
C(6)	3362(2)	3117(2)	346(1)	29(1)
C(11)	6874(2)	−40(2)	2170(1)	29(1)
C(12)	5284(2)	722(3)	2362(1)	39(1)
C(13)	3149(2)	661(2)	1556(1)	32(1)
C(14)	3776(2)	−284(2)	1025(1)	26(1)

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Ni–O(1)	2.0925(1)	Ni–O(3)	2.0451(1)
Ni–O(5)	2.0834(1)	Ni–N(1)	2.058(2)
Ni–N(3)	2.101(2)	Ni–N(5)	2.119(1)
S(1)–C(1)	1.737(2)	S(1)–C(2)	1.727(2)
S(2)–C(5)	1.722(2)	S(2)–C(6)	1.734(2)
O(1)–C(11)	1.270(2)	O(2)–C(11)	1.231(2)
O(3)–C(14)	1.258(2)	O(4)–C(14)	1.247(2)
N(1)–C(1)	1.319(2)	N(1)–C(3)	1.389(3)
N(2)–C(1)	1.334(3)	N(3)–C(6)	1.318(2)
N(3)–C(4)	1.389(3)	N(4)–C(6)	1.340(3)
N(5)–C(13)	1.470(2)	N(5)–C(12)	1.471(2)
C(2)–C(3)	1.345(3)	C(3)–C(4)	1.463(3)
C(4)–C(5)	1.348(3)	C(11)–C(12)	1.524(3)
C(13)–C(14)	1.524(2)		
O(1)–Ni–O(3)	88.26(5)	O(1)–Ni–O(5)	91.26(5)
O(1)–Ni–N(1)	95.26(6)	O(1)–Ni–N(3)	171.65(6)
O(1)–Ni–N(5)	82.10(5)	O(3)–Ni–O(5)	89.33(5)
O(3)–Ni–N(1)	176.45(6)	O(3)–Ni–N(3)	96.41(6)
O(3)–Ni–N(5)	80.98(6)	O(5)–Ni–N(1)	91.00(6)
O(5)–Ni–N(3)	95.69(6)	O(5)–Ni–N(5)	168.39(6)
N(1)–Ni–N(3)	80.04(6)	N(1)–Ni–N(5)	99.06(6)
N(3)–Ni–N(5)	91.77(6)		

those reported previously. This may be due to the aromatic stacking interaction between thiazole rings as mentioned below.

Within the twisted DABT moiety, the N(3)-thiazole ring tilts to the coordination plane formed by O(1), O(3), N(1) and N(3) atoms with a large dihedral angle of

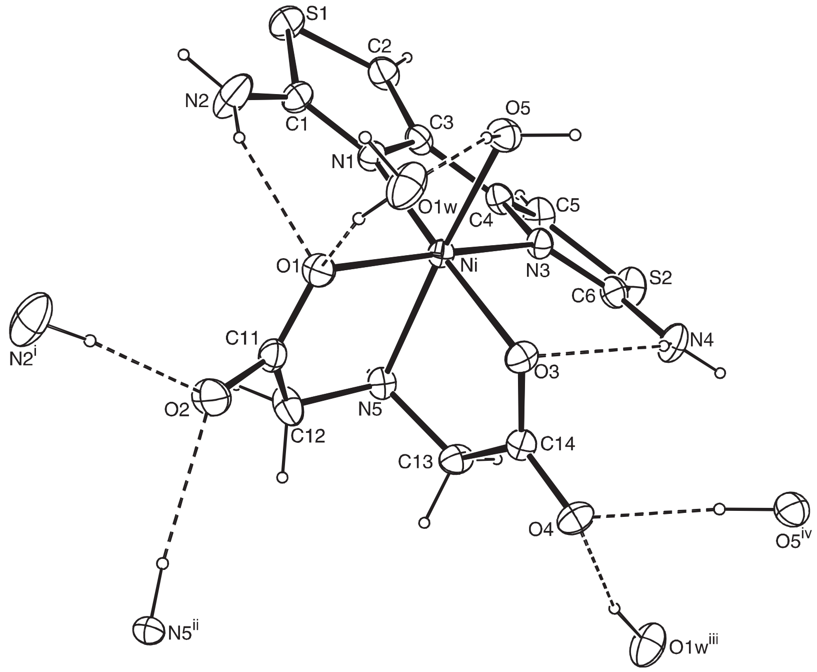

Figure 1. The molecular structure of the complex with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding. Symmetry codes: (i) $2-x, -0.5+y, 0.5-z$; (ii) $1-x, -0.5+y, 0.5-z$; (iii) $-1+x, y, z$; (iv) $1-x, -y, -z$.

Table 3. A comparison of geometric parameters of DABT.

Complex	C3–C4 bond distance (Å)	Dihedral angle (°)	Reference
Cr(DABT)(IDA)Cl(H_2O)	1.454	5.52	[8]
Mn(DABT)ODA(H_2O)	1.457	4.57	[9]
$Co(DABT)_2Cl_2$	1.454, 1.456	2.11, 10.29	[10]
Co(DABT)ODA(H_2O)	1.459	5.54	[11]
$Ni(DABT)_2(SCN)Cl$	1.453, 1.465	5.05, 8.75	[12]
$Ni(DABT)_2Cl_2$	1.444, 1.458	1.63, 11.11	[13]
$Ni(DABT)_2$Phthalate	1.459, 1.453	7.90, 9.73	[14]
Ni(DABT)IDA(H_2O)	1.463	20.04	this work
Cu(DABT)ODA(H_20)	1.466	6.46	[15]
$Cu(DABT)Cl_2$	1.468	1.82	[16]
$Cd(DABT)_2Cl_2$	1.460, 1.464	8.38, 10.23	[17]

23.23(7)°; and the Ni(II) atom deviates from the N(3)-thiazole planes by 0.703(4) Å. The N(1)-thiazole ring is nearly coplanar with the coordination plane, the dihedral angle being 12.08(8)°; and the atomic deviation of the Ni atom is 0.259(3) Å. This difference is also due to the aromatic stacking between N(3)-thiazole rings. Two N(3)-thiazole rings from neighboring complex molecules, related by an inversion centre at (0.5, 0.5, 0.0), are parallel and overlap with a short separation of 3.475(7) Å, which clearly suggests the existence of aromatic bonding, as shown in figure 2. No aromatic stacking is observed between the neighboring N(1)-thiazole rings.

The tridentate IDA dianion chelates to a Ni(II) atom in a facial configuration, as usually observed for IDA in transition metal complexes [8]. Both chelating

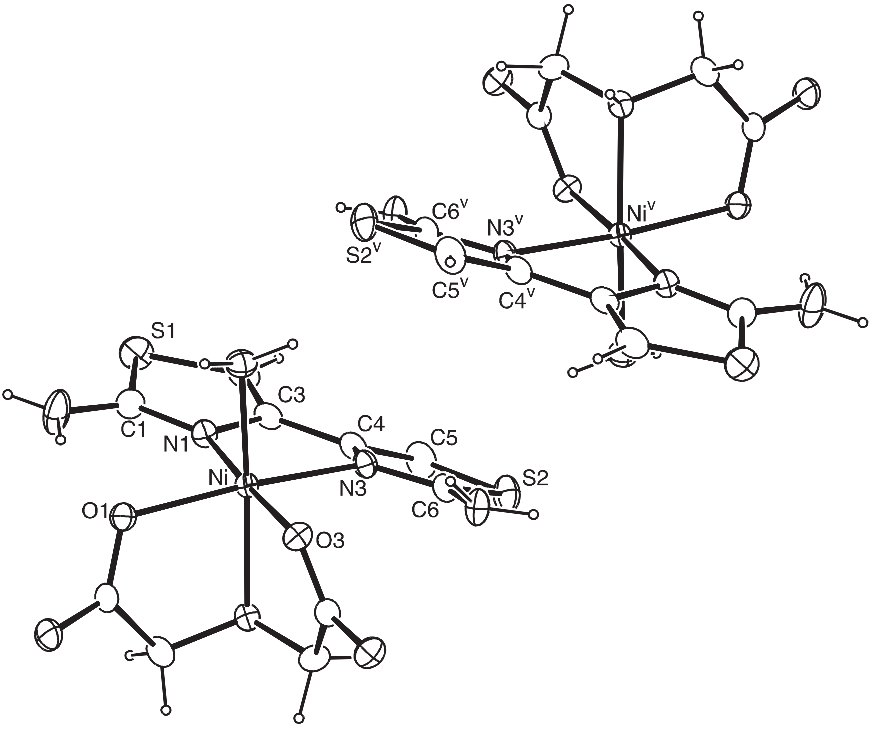

Figure 2. Aromatic stacking between neighboring N(3)–thiazole rings. Symmetry code: (v) $1-x$, $1-y$, $-z$.

Table 4. Hydrogen bonding parameters (Å, °) for the complex.

Donor–H–Acceptor	D–H	H···A	D···A	D–H–A
O(1W)–H(1A)···O(1)	0.865	1.949	2.729(2)	149.4
O(1W)–H(1B)···O(4)^{vi}	0.878	1.851	2.707(2)	164.5
N(2)–H(2A)···O(2)^{vii}	0.860	1.978	2.835(3)	175.0
N(2)–H(2B)···O(1)	0.860	2.174	2.943(3)	148.7
N(4)–H(4A)···O(3)	0.860	2.380	3.068(2)	137.3
N(4)–H(4A)···O(3)^{iv}	0.860	2.392	3.004(2)	128.6
N(4)–H(4B)···O(1W)^{iv}	0.860	2.119	2.876(2)	146.5
O(5)–H(5A)···O(1W)	0.910	1.969	2.834(2)	158.2
O(5)–H(5B)···O(4)^{iv}	0.927	1.889	2.808(2)	170.6
N(5)–H(5C)···O(2)^{viii}	0.910	2.185	3.060(2)	161.1

Symmetry codes: (iv) $1-x$, $-y$, $-z$; (vi) $1+x$, y, z; (vii) $2-x$, $0.5+y$, $0.5-z$; (viii) $1-x$, $0.5+y$, $0.5-z$.

five-membered rings of IDA have a similar envelope conformation. The C(11) atom is in the flap position of the O(1)-ring and out of the mean plane formed by the other four atoms by 0.274(3) Å, while the N(5) atom is in the flap position of the O(3)-ring and out of the mean plane by 0.514(3) Å. Carboxyl groups of IDA coordinate to the Ni(II) atom as monodentates. The uncoordinated carboxyl O(2) atom is hydrogen bonded to an amino and an imino group of adjacent complex molecules, while the uncoordinated carboxyl O(4) atom is hydrogen bonded to

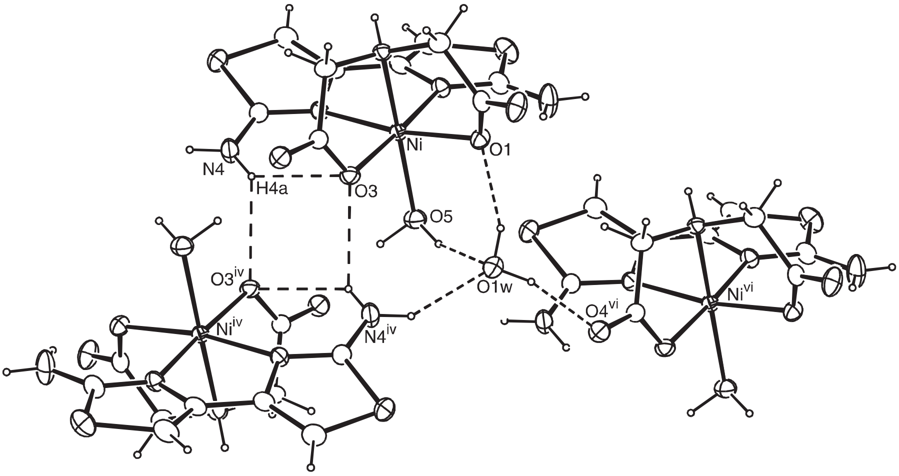

Figure 3. The hydrogen bond network holds complex molecules together to form a supramolecular structure. Symmetry codes: (iv) $1-x, -y, -z$; (vi) $1+x, y, z$.

lattice water and coordinated water of a neighboring complex molecule, as shown in figure 1.

An extensive hydrogen bond network occurs in the crystal (table 4). The amino groups of DABT are hydrogen bonded to coordinated carboxyl oxygen atoms. Each lattice water molecule simultaneously links three neighboring complex molecules, while three-centered hydrogen bonds hold adjacent complex molecules together (figure 3), the sum of three angles at the H4a atom being 357.1°.

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