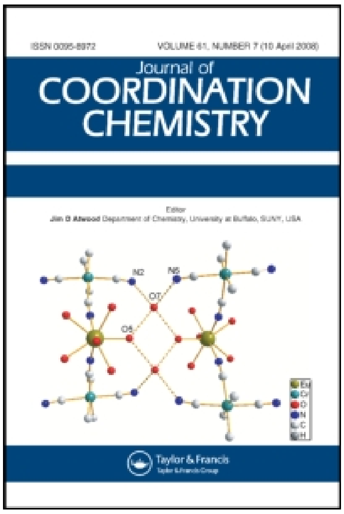

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Synthesis and crystal structure of aqua(dimethylbithiazole)oxydiacetatonickel(II) trihydrate

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The title complex, $Ni(C_8H_8N_2S_2)(C_4H_4O_5)(H_2O)\cdot 3H_2O$, was synthesized and its crystal structure determined by X-ray diffraction methods. Two crystallographically independent complex molecules are present in the asymmetric unit. They have similar octahedral coordination geometries, formed by a bidentate dimethylbithiazole (dMbt), a tridentate oxydiacetate dianion (ODA) and a coordinated water molecule. The tridentate ODA ligand displays an unusual *facial* configuration. A partially overlapped arrangement of nearly parallel dMbt ligands of neighbouring molecules is observed in the crystal, the shortest centroid distance of 3.555(3) Å between thiazole rings suggesting the existence of aromatic π–π stacking.

Keywords: Nickel(II); Dimethylbithiazole; Oxydiacetate; Crystal structure; Aromatic stacking

1. Introduction

Transition metal complexes of 2,2′-diamine-4,4′-bithiazole (dAbt) or its derivatives have attracted attention for several years because of their potential application in many fields. For example, the Co(II) and Ni(II) complexes are effective inhibitors of DNA synthesis in tumor cells [1, 2], and multinuclear Fe(II) and Cu(II) complexes with dAbt Schiff bases are excellent soft magnetic materials [3, 4]. A series of metal complexes incorporating dAbt has been prepared and their X-ray structures determined [5, 6]. As a part of a continuing investigation of metal complexes with bithiazole, a Ni(II) complex of dimethylbithiazole (dMbt) has been prepared and its X-ray structure is described below.

2. Experimental

2.1. *Synthesis*

All reagents were commercially available and of analytical grade. $NiCl_2\cdot 6H_2O$ (0.24 g, 1 mmol) and dMbt (0.20 g, 1 mmol) were added to an aqueous

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solution ($15\,\mathrm{cm}^3$) containing oxydiacetic acid (0.14 g, 1 mmol) and Na_2CO_3 (0.11 g, 1 mmol). The solution was refluxed for 2.5 h. After cooling to room temperature, the solution was filtered twice. Single crystals of the title compound were obtained after 3 weeks.

C, H and N contents were determined using a Carlo-Erba 1160 instrument. Anal. Calcd for $C_{12}H_{14}N_2NiO_6S_2 \cdot 3H_2O$ (%): C, 31.36; N, 6.10; H, 4.36. Found: C, 31.65; N, 6.45; H, 4.49. The IR spectrum of the complex (KBr pellet) was recorded in the 4000–400 cm^{-1} region using a Nicolet 5DX FT-IR spectrophotometer.

2.2. *Crystal structure*

X-Ray diffraction intensities were collected on a Rigaku R-AXIS RAPID diffractometer at room temperature. The crystal structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on F^2 [7]. H atoms on lattice water molecules were located in a difference Fourier map and refined isotropically using a riding model with $U_{\mathrm{iso}}(\mathrm{H}) = 0.05\,\text{Å}^2$. Methyl H atoms were located in calculated positions with C–H = 0.96 Å and torsion angles refined from electron densities with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}$ of the carrier atoms. Other H atoms were placed in calculated positions, with C–H = 0.93 Å (aromatic) or 0.97 Å (methylene), and were included in the final cycles of refinement in riding mode with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ of the carrier atoms. Crystal data and refinement conditions are summarized in table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 2.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{12}H_{14}N_2NiO_6S_2 \cdot 3H_2O$
Formula weight	459.13
Crystal size (mm^3)	0.20 × 0.19 × 0.13
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions (Å)	$a = 21.450(1)$ $b = 7.144(1)$ $c = 24.616(1)$
V (Å^3)	3772.3(6)
Z	8
Density (calculated) ($\mathrm{g\,cm}^{-3}$)	1.617
Absorption coefficient (mm^{-1})	1.297
$F(000)$	1904
θ range for data collection (°)	1.6 to 25.0
Reflections collected	25874
Independent reflections	6575
Observed reflections [$I > 2\sigma(I)$]	5777
Parameters	473
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0761$
R indices (all data)	$R_1 = 0.0402$, $wR_2 = 0.0791$
Largest diff. peak and hole ($\mathrm{e}\,\text{Å}^{-3}$)	0.57 and −0.35

Table 2. Atomic coordinates and equivalent isotropic displacement parameters.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Ni1	0.79093(3)	0.25579(6)	0.59157(2)	0.0233(2)
S1	0.96897(5)	0.1710(2)	0.49017(6)	0.0406(3)
S2	0.69201(7)	0.4035(2)	0.42827(7)	0.0569(4)
O1	0.8293(1)	0.2085(4)	0.6658(1)	0.0368(9)
O2	0.8143(2)	0.2577(4)	0.7540(2)	0.043(2)
O3	0.7087(2)	0.2523(3)	0.6420(2)	0.030(1)
O4	0.7663(1)	−0.0161(4)	0.5829(1)	0.0374(9)
O5	0.7038(2)	−0.2404(4)	0.6142(3)	0.055(2)
O11	0.8041(1)	0.5345(4)	0.6029(1)	0.0381(9)
N1	0.8683(2)	0.2303(4)	0.5417(2)	0.027(1)
N2	0.7501(2)	0.3268(4)	0.5152(1)	0.031(1)
C1	0.7953(3)	0.2525(5)	0.7056(2)	0.027(2)
C2	0.7305(2)	0.3119(7)	0.6945(2)	0.038(1)
C3	0.6830(2)	0.0676(5)	0.6419(2)	0.040(1)
C4	0.7206(2)	−0.0735(5)	0.6102(2)	0.0330(1)
C10	0.9541(2)	0.1275(8)	0.6024(2)	0.056(2)
C11	0.9267(2)	0.1791(6)	0.5493(2)	0.033(1)
C12	0.9061(3)	0.2403(5)	0.4542(3)	0.036(2)
C13	0.8573(3)	0.2628(5)	0.4870(3)	0.029(2)
C14	0.7934(2)	0.3170(6)	0.4733(2)	0.034(2)
C15	0.7695(2)	0.3538(6)	0.4229(2)	0.046(1)
C16	0.6951(2)	0.3741(5)	0.4978(2)	0.041(2)
C17	0.6393(2)	0.4043(7)	0.5329(2)	0.059(2)
Ni2	0.53832(3)	0.26095(6)	0.85918(2)	0.0239(2)
S3	0.43974(6)	0.1031(2)	1.02078(7)	0.0542(4)
S4	0.71678(5)	0.3418(1)	0.96016(6)	0.0403(3)
O6	0.5765(1)	0.3231(4)	0.7849(1)	0.0366(9)
O7	0.5640(2)	0.2641(4)	0.6967(2)	0.039(2)
O8	0.4575(2)	0.2655(3)	0.8082(2)	0.028(1)
O9	0.5124(1)	0.5312(3)	0.8688(1)	0.0373(9)
O10	0.4509(2)	0.7569(4)	0.8392(2)	0.045(2)
O12	0.5535(1)	−0.0178(3)	0.8452(1)	0.0378(9)
N3	0.4983(2)	0.1853(5)	0.9340(2)	0.034(1)
N4	0.6169(2)	0.2843(5)	0.9080(2)	0.026(1)
C5	0.5465(3)	0.2691(6)	0.7445(3)	0.036(2)
C6	0.4785(2)	0.2022(7)	0.7555(2)	0.035(1)
C7	0.4314(2)	0.4528(5)	0.8067(2)	0.040(1)
C8	0.4687(2)	0.5908(5)	0.8406(2)	0.034(1)
C20	0.3874(2)	0.1035(7)	0.9162(2)	0.058(2)
C21	0.4428(2)	0.1344(5)	0.9517(2)	0.038(1)
C22	0.5165(3)	0.1581(6)	1.0257(2)	0.047(1)
C23	0.5403(2)	0.1976(6)	0.9766(2)	0.032(1)
C24	0.6024(3)	0.2511(4)	0.9624(2)	0.026(2)
C25	0.6526(3)	0.2750(6)	0.9965(3)	0.040(2)
C26	0.6745(2)	0.3337(5)	0.9009(2)	0.031(1)
C27	0.7035(2)	0.3791(8)	0.8477(2)	0.055(2)
O1W	0.7635(2)	−0.0870(5)	0.7957(2)	0.067(1)
O2W	0.6073(2)	−0.3571(5)	0.6806(2)	0.064(1)
O3W	0.8950(2)	0.6817(6)	0.6659(2)	0.079(2)
O4W	0.5197(2)	−0.0775(5)	0.6502(1)	0.063(1)
O5W	0.3508(2)	0.8689(5)	0.7760(2)	0.068(1)
O6W	0.6384(2)	−0.1606(7)	0.7802(2)	0.109(2)

3. Results and discussion

Two crystallographically independent complex molecules, Mol1 and Mol2, occur in the asymmetric unit of the title crystal. Their molecular structures are shown in figure 1.

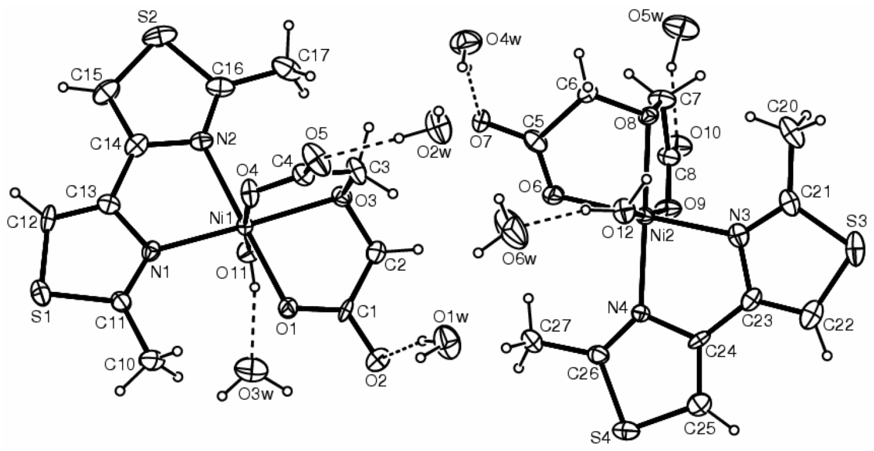

Figure 1. The molecular structure of the complex with the atom numbering scheme. Dashed lines indicate hydrogen bonding.

Table 3. Selected bond lengths (Å) and angles (°) for the complex.

Ni1–O1	2.032(3)	Ni1–O3	2.158(4)
Ni1–O4	2.024(3)	Ni1–O11	2.030(3)
Ni1–N1	2.072(5)	Ni1–N2	2.136(3)
Ni2–O12	2.047(2)	Ni2–N3	2.103(4)
Ni2–N4	2.076(4)	Ni2–O9	2.023(2)
Ni2–O6	2.053(3)	Ni2–O8	2.141(4)
O1–Ni1–O3	79.2(2)	O1–Ni1–O4	92.4(1)
O1–Ni1–O11	89.0(1)	O1–Ni1–N1	101.2(2)
O1–Ni1–N2	175.8(1)	O3–Ni1–O4	80.6(1)
O3–Ni1–O11	92.4(1)	O3–Ni1–N1	174.1(1)
O3–Ni1–N2	100.0(2)	O4–Ni1–O11	172.1(1)
O4–Ni1–N1	93.6(1)	O4–Ni1–N2	91.6(1)
O11–Ni1–N1	93.2(1)	O11–Ni1–N2	86.9(1)
N1–Ni1–N2	80.1(2)	N3–Ni2–N4	81.1(2)
O6–Ni2–O8	78.4(1)	O6–Ni2–O9	90.5(1)
O6–Ni2–O12	89.9(1)	O6–Ni2–N3	177.5(1)
O6–Ni2–N4	100.1(2)	O8–Ni2–O9	80.3(1)
O8–Ni2–O12	92.6(1)	O8–Ni2–N3	100.7(2)
O8–Ni2–N4	174.5(1)	O9–Ni2–O12	172.7(1)
O9–Ni2–N3	91.7(1)	O9–Ni2–N4	94.5(1)
O1–Ni2–N3	87.8(1)	O12–Ni2–N4	92.7(1)

Both Ni(II) complex molecules have similar distorted octahedral coordination geometries (table 3). The tridentate oxydiacetate dianion (ODA) chelates to the Ni(II) atom in a *facial* configuration. Two coordination planes formed by the carboxyl O and ether O atoms are nearly perpendicular to each other, dihedral angles being 85.8(1)° (Mol1) and 81.3(1)° (Mol2), respectively. Of the two chelate rings of ODA, one is planar but the other has an envelope configuration with the Ni atom lying at the flap position and lying out of the mean plane formed by the other four atoms by 0.716(6) (Mol1) and 0.832(6) Å (Mol2). ODA usually chelates a transition metal anion in the *meridional* configuration, as in [Ni(ODA)(dAbt)(H_2O)] [8]. The Ni–O(ether) bond distances of 2.158(4) (Mol1) and 2.141(4) Å (Mol2) are significantly longer than the

Ni–O(carboxyl) bond distances (table 3); this too differs from the situation found in [Ni(ODA)(dAbt)(H_2O)] [8].

The two thiazole rings of the same dMbt ligand are coplanar, maximum atomic deviations being 0.029(2) (in Mol1) and 0.014(2) Å (in Mol2). Aromatic π–π stacking is observed between dMbt ligands of neighbouring complexes, as shown in figure 2. The shortest centroid distance is 3.555(3) Å between S1-thiazole and $\mathrm{S4^i}$-thiazole rings [symmetry code (i); $3/2-x$, $-1/2+y$, $-1/2+z$]. An extensive hydrogen network occurs in the crystal. Uncoordinated carboxyl oxygen atoms are hydrogen bonded both with coordinated and lattice water molecules (table 4). Through the intermolecular hydrogen bonding, complex molecules link to form a supramolecular structure consisting of hydrophilic and hydrophobic layers, as shown in figure 3.

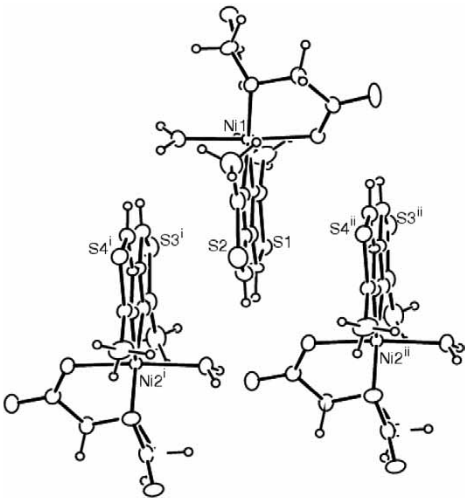

Figure 2. A view of the parallel arrangement of neighbouring bMbt ligands. Symmetry codes are (i): $3/2-x$, $-1/2+y$, $-1/2+z$; (ii): $3/2-x$, $1/2+y$, $-1/2+z$.

Table 4. Hydrogen bonding parameters (Å, °).

D–H···A	D–H	H···A	D···A	D–H–A
O1W–H1A···O2	0.85	2.06	2.882(5)	164
O1W–H1B···O5W^{a}	0.94	1.85	2.792(5)	175
O2W–H2A···O5	0.86	1.94	2.766(7)	159
O2W–H2B···O7^{b}	0.87	2.09	2.889(5)	154
O3W–H3A···O5W^{c}	0.97	2.14	2.893(6)	134
O3W–H3B···O4W^{a}	0.89	1.92	2.803(5)	179
O4W–H4A···O7	0.86	2.00	2.858(5)	172
O4W–H4B···O2W	0.86	1.99	2.843(5)	170
O5W–H5A···O10	0.90	1.91	2.770(6)	159
O5W–H5B···O2^{d}	0.92	1.95	2.832(5)	160
O6W–H6A···O1W	0.86	2.01	2.762(6)	145
O6W–H6B···O2W	0.85	2.10	2.903(6)	157
O11–H11A···O3W	0.86	1.86	2.704(5)	168
O11–H11B···O5^{e}	0.86	2.10	2.701(5)	127
O12–H12A···O10^{b}	0.93	1.81	2.730(5)	173
O12–H12B···O6W	0.83	1.85	2.631(6)	156

Symmetry codes are (a): $1/2+x$, $1/2-y$, z; (b): x, $-1+y$, z; (c): $1/2+x$, $3/2-y$, z; (d): $-1/2+x$, $3/2-y$, z; (e): x, $1+y$, z.

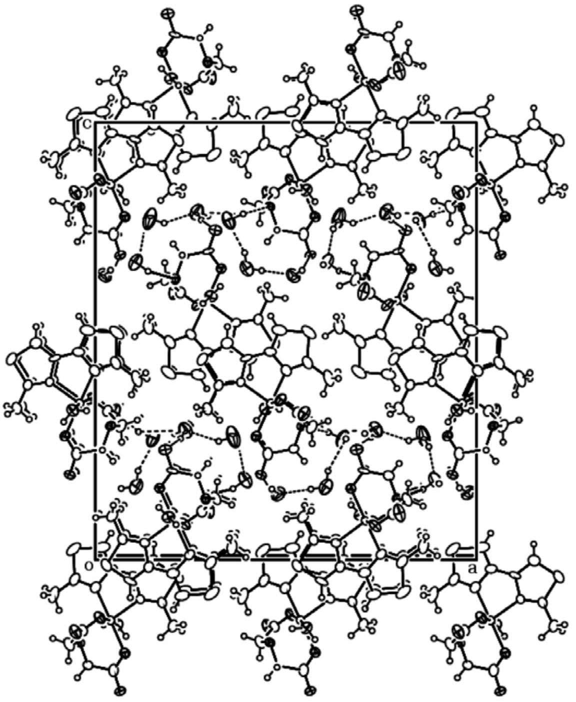

Figure 3. Unit cell packing showing hydrogen bonding.

The IR spectrum of the complex was assigned based on the crystal structure. Stretching vibrations of the carboxyl group were observed at 1618 [ν_{as}(COO)] and 1407 cm^{-1} [ν_s(COO)]. The $\Delta\nu$ value of 211 cm^{-1} agrees with the monodentate coordination mode of the carboxyl group [9]. The stretching vibration of water appeared at 3405 cm^{-1}. Compared to values of 3650–3600 cm^{-1} found for the "free" hydroxyl group, the higher energy $\nu_{(OH)}$ indicates the participation of the hydroxyl groups in hydrogen bonding.

Supplementary material

Full crystallographic data have been deposited in CCDC with deposition number CCDC268410.

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