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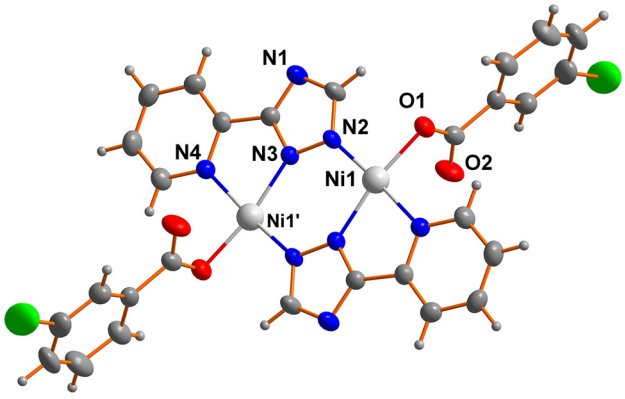
Hydrothermal synthesis, crystal structure of [K3：N1:N2:N4-3-(pyridin-2-yl)-1,2,4-triazole] binuclear Ni(II) complex[$Ni_2(C_7H_5N_4)2(C_7H_4ClO_2)_2$]



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Abstract

$C_{28}H_{18}Cl_2Ni_2N_8O_4$, *monoclinic*, $P2_1/c$ (no. 14), a = 15.162(3) Å, b = 9.6548(16) Å, c = 9.6957(17) Å, β = 101.038(3)°, V = 1393.1(4) Å^3, Z = 2, *GooF*=1.035, $R_{gt}(F)$ = 0.0364, $wR_{ref}(F^2)$ = 0.1016, T = 296 K.

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Table 1, contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Green block
Size	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.60 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6990, 2557, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2082
$N(param)_{refined}$:	199
Programs:	SHELX[1–3]

1 Source of material

An amount of 0.2 mmol(about 34.53 mg) 3-chlorobenzoic acid and, 0.1 mmol 3-(pyridin-2-yl)-1,2,4-triazole(HPT) (about 14.60 mg) and 0.2 mmol (about 18.54 mg) nickel hydroxide were dissolved in 9 mL water and 3 mL ethanol. The pH value was adjusted to about 5~6 with 0.1 M NaOH solution. The reaction mixture was refluxed for nearly 1 h under stirring. After that, the mixture was placed in a 20 mL hydrothermal auto-clave. The vessel was sealted and heated at 140°C for 72 h. Afterwards the system was cooled to room temperature. The blue granulate single crystals suitable for crystal structure measurement were obtain.

2 Experimental details

The H atoms bound to C atoms were placed in idealized positions and treated as riding on their parent atoms, with d(C–H) = 0.96 Å(methylene), with U_{iso}(H) = 1.5U_{eq}(C), and d(C–H) = 0.93 Å(aromtic), with U_{iso}(H) = 1.2U_{eq}(C).

3 Comment

Nickel is a necessary element in living organisms and can become the active center of biological enzymes, so the simulation and study of nickel enzyme structure has always been an important research topic in the field of bioinorganic chemistry.[4,5] In recent years, with the expansion of the research scope of nickel complexes, the application reports mainly focus on molecular magnets, superoxide dismutase, biological activity and catalysis.[6,7] In addition, carboxylic acid complexes and multi-dentate nitrogen-containing complexes are mainly studied.[8,9] These ligands form mononuclear,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Ni1	0.59068 (2)	−0.94190 (4)	1.16903 (4)	0.02527 (15)
Cl2	1.05532 (9)	−0.64303 (15)	1.1107 (2)	0.1075 (6)
O1	0.67235 (14)	−0.7897 (2)	1.2349 (2)	0.0366 (5)
O2	0.75094 (18)	−0.9140 (2)	1.1095 (3)	0.0498 (7)
N1	0.49163 (19)	−0.6587 (3)	0.8525 (3)	0.0428 (7)
N2	0.53423 (16)	−0.8338 (2)	1.0028 (3)	0.0299 (6)
N3	0.47300 (16)	−0.8834 (3)	0.8923 (2)	0.0282 (6)
N4	0.34982 (16)	−0.9311 (2)	0.6711 (3)	0.0302 (6)
C1	0.8183 (2)	−0.7096 (3)	1.2189 (3)	0.0325 (7)
C2	0.3383 (2)	−0.6944 (3)	0.5965 (3)	0.0358 (7)
H2	0.357744	−0.603184	0.609999	0.043*
C3	0.9613 (3)	−0.5271 (4)	1.2904 (5)	0.0644 (13)
H3	1.009390	−0.466428	1.314353	0.077*
C4	0.4489 (2)	−0.7767 (3)	0.8078 (3)	0.0301 (7)
C5	0.2693 (2)	−0.7298 (4)	0.4866 (4)	0.0408 (8)
H5	0.241568	−0.662199	0.424747	0.049*
C6	0.3772 (2)	−0.7976 (3)	0.6848 (3)	0.0295 (7)
C7	0.5437 (2)	−0.7003 (3)	0.9742 (4)	0.0407 (8)
H7	0.582509	−0.641248	1.032658	0.049*
C8	0.7430 (2)	−0.8126 (3)	1.1836 (3)	0.0331 (7)
C9	0.2421 (2)	−0.8652 (4)	0.4697 (4)	0.0425 (9)
H9	0.196738	−0.890867	0.395305	0.051*
C10	0.2830 (2)	−0.9626 (3)	0.5646 (3)	0.0369 (8)
H10	0.263261	−1.053895	0.554127	0.044*
C11	0.8880 (3)	−0.5176 (4)	1.3540 (4)	0.0602 (11)
H11	0.886798	−0.449918	1.421908	0.072*
C12	0.8159 (2)	−0.6073 (4)	1.3185 (4)	0.0425 (8)
H12	0.766171	−0.599005	1.361223	0.051*
C13	0.9622 (2)	−0.6282 (4)	1.1906 (5)	0.0563 (11)
C14	0.8912 (2)	−0.7192 (4)	1.1535 (4)	0.0439 (9)
H14	0.892556	−0.786190	1.085120	0.053*

binuclear or multinuclear complexes through coordination bonds, or form one-dimensional, two-dimensional or three-dimensional polymers.[10,11] 3-chlorobenzoic acid also acts as an aromatic carboxylic acid ligand, which can coordinate with metal ions due to its multiple coordination sites.

As shown in Fig. 1, complex **1** consists of two Ni(II) ion, two *m*-chlorobenzoate anions, and two 3-(pyridin-2-yl)-1,2,4-triazole(HPT) anions. The title complex is located around an inversion center. Each Ni(II) ion is coordinated with three nitrogen atoms from two HPT molecules, and two oxygen atoms from *m*-chlorobenzoic acid anions. In the NiN_3O_2 tetragonal pyramid O(1), N(2), N(3^1) and N(4^1) locate at equator plane, but O(2) occupy the axial positions. Bond angles O(1)–Ni(1)–N(2), N(2)–Ni(1)–N(3^1), N(3^1)- Ni(1)–N(4^1) and N(4^1)–Ni(1)–O(1) are 91.01(9)°, 95.46(9)°, 80.54(10)° and 92.49(10)°, respectively. The sum of angles is 359.50°(close to 360°), suggesting a planar nature of O(1), N(2), N(3^1), N(4^1) and Ni(1) with planar equation of 12.137 x + −2.094 y + −6.419 z = 2.4974, which the average deviation of all the atoms is 0.0304 Å. The bond lengths Ni1–O1 and Ni1–O2 are 1.949(2) and 2.617(3) Å,[12] which the latter is much greater than the former and indicates that Ni1–O2 forms a weak coordination. The bond lengths Ni1–N2, Ni1–N3^1 and Ni1–N4^1 are 1.973(2), 1.977(2) and 2.045(3) Å, respectively, The average bond lengths of Ni1–N is 1.966 Å, which are in the normal ranges.[13] They are a little bit shorter than similar complex[{[Ni(4,4′-bipy)(3,5–DMBA)$_2$ (CH_3OH)$_2$] [Ni(4,4′-bipy)(3,5–DMBA)$_2$ (H_2O)$_2$]}$_n$ Ni–N = 2.155 Å].[14] Otherwise, the shortest center distance between aromatic cycles of *m*-chlorobenzoate group is 3.707 Å, indicating π-π stacking interaction between the aromatic cycles.[12]

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