Crystal structure of tetraaqua dinitrato-κ^2O,O'-4,4',6,6'-tetramethyl-2,2'-bipyrimidine-$\kappa^4N,N':N'',N'''$ dinickel(II) dinitrate, $C_6H_{11}N_4NiO_8$

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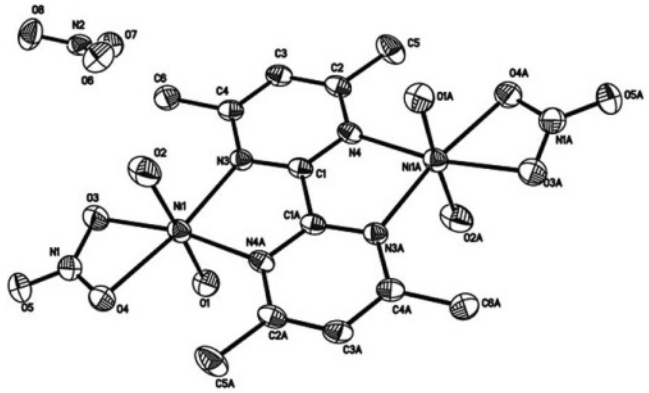

Abstract

$C_6H_{11}N_4NiO_8$, monoclinic, $P2_1/n$ (no. 14), a = 9.773(2) Å, b = 10.614(2) Å, c = 11.485(2) Å, β = 92.479(2)°, V = 1190.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.0332, $wR_{ref}(F^2)$ = 0.0959, T = 296 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.18×0.29×0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.75 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8560, 2206
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1705
$N(param)_{refined}$:	174
Programs:	SHELX [6]

Source of material

A mixture of $Ni(OAc)_2{\cdot}6H_2O$ (0.116 g, 0.4 mmol) and *tmbpm* (4,4',6,6'-tetramethyl-2,2'-bipyrimidine, 0.043 g, 0.2 mmol) in H_2O (12 mL) was stirred for 30 min at room temperature. Then the solution was transferred and sealed in a 20 mL Teflon-lined stainless vessel which was heated at 140 °C for three days. After the solution cooled to room temperature at a rate of 2.3 °C/h, green block crystals of the title compound were obtained.

Experimental details

The hydrogen atoms were assigned with common isotropic displacement factors U_{iso}(H) = 1.2 times U_{eq}(aryl C), or U_{iso}(H) = 1.5 times U_{eq}(methyl C or water O) and included in the final refinement by using geometrical restraints, with C–H = 0.93 Å (aryl) or C–H = 0.96 Å (methyl), and O–H = 0.84 Å.

Discussion

2,2'-bipyrimidine (*bpm*) has been extensively used in the development of metal complexes [1, 2]. As a versatile ligand, *bpm* is able to coordinate metal ions in a bidentate or bis-bidentate bridging mode, leading to mono or polynuclear complexes [3]. A large number of uncommon magnetic systems have been reported as a consequence of the growing research on the magnetic properties of *bpm*-bridged complexes [4, 5]. There is a growing interest in bridging ligands to construct metal complexes with interesting properties for potential application. This contribution is part of a study which investigates the factors influencing the coordination mode of the ligands and control the final structure of the complexes. We select 4,4',6,6'-tetramethyl-2,2'-bipyrimidine (*tmbpm*), the derivatives of *bpm*, to design the expect complexes. The structure of the title compound consists of discrete $[Ni_2(tmbpm)(NO_3)_2(H_2O)_4]^{2+}$ units, and NO_3^- anions (Fig.). The two Ni(II) atoms are bridged by a *tmbpm* ligand. Each Ni^{2+} is in a slightly distorted octahedral environment: two nitrogen atoms from the *tmbpm* (2.063 Å for Ni1–N3 and 2.078 Å for Ni1–N4) and two oxygen atoms from the nitrate moiety (2.092 Å for Ni1–O3 and 2.122 Å for Ni1–O5) build the equatorial plane, while the axial position are occupied by two water oxygen atoms (2.083 Å for Ni1–O1 and 2.031 Å for Ni1–O2). The Ni-(*tmbpm*)-Ni unit is almost planar with the largest deviation of 0.269 Å for C6, and the Ni–Ni distance is 5.518 Å. The hydrogen bonding interactions play an important role in stabilizing the title crystal structure of the title compound. The $[Ni_2(tmbpm)(NO_3)_2(H_2O)_4]^{2+}$ units and the NO_3^- anions are linked by hydrogen bonds to form a three-dimensional supramolecular structure.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1W)	4*e*	0.3201	–0.0610	0.9103	0.080
H(2W)	4*e*	0.2972	0.0352	0.8325	0.080
H(3W)	4*e*	–0.1540	–0.1390	0.7843	0.102
H(4W)	4*e*	–0.0976	–0.2444	0.7375	0.102
H(3)	4*e*	–0.0895	0.3423	0.8094	0.054
H(5A)	4*e*	–0.2237	0.3540	1.0695	0.099
H(5B)	4*e*	–0.1527	0.4450	0.9832	0.099
H(5C)	4*e*	–0.0719	0.3968	1.0953	0.099
H(6A)	4*e*	0.0829	0.1605	0.6459	0.087
H(6B)	4*e*	–0.0536	0.2372	0.6301	0.087
H(6C)	4*e*	–0.0575	0.0896	0.6312	0.087

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*e*	0.09529(4)	–0.10752(3)	0.80034(3)	0.0460(3)	0.0298(2)	0.0480(3)	0.0019(2)	0.0013(2)	–0.0039(2)
O(1)	4*e*	0.2909(2)	–0.0402(2)	0.8448(2)	0.052(1)	0.049(1)	0.059(1)	–0.005(1)	–0.000(1)	–0.003(1)
O(2)	4*e*	–0.0934(2)	–0.1671(2)	0.7431(2)	0.056(1)	0.049(2)	0.098(2)	–0.001(1)	–0.009(1)	–0.026(1)
O(3)	4*e*	0.1521(3)	–0.0857(2)	0.6280(2)	0.070(2)	0.046(2)	0.057(1)	0.014(1)	0.002(1)	–0.001(1)
O(4)	4*e*	0.1887(2)	–0.2618(2)	0.7171(2)	0.065(2)	0.041(1)	0.056(1)	0.009(1)	–0.002(1)	–0.003(1)
O(5)	4*e*	0.2667(3)	–0.2331(3)	0.5428(2)	0.089(2)	0.088(2)	0.052(1)	0.031(2)	0.002(1)	–0.023(1)
O(6)	4*e*	0.1127(3)	0.3825(3)	0.4320(3)	0.090(2)	0.063(2)	0.085(2)	–0.021(2)	–0.011(2)	0.015(2)
O(7)	4*e*	0.2099(3)	0.5575(2)	0.3902(2)	0.074(2)	0.044(2)	0.090(2)	–0.007(1)	–0.009(1)	–0.011(1)
O(8)	4*e*	0.1422(3)	0.4318(3)	0.2537(3)	0.130(3)	0.060(2)	0.066(2)	–0.001(2)	–0.022(2)	–0.008(1)
N(1)	4*e*	0.2052(3)	–0.1946(3)	0.6248(2)	0.057(2)	0.054(2)	0.052(2)	0.010(2)	–0.009(1)	–0.011(2)
N(2)	4*e*	0.1535(3)	0.4574(3)	0.3580(3)	0.058(2)	0.038(2)	0.074(2)	0.007(1)	–0.014(2)	–0.004(2)
N(3)	4*e*	0.0074(2)	0.0582(2)	0.8538(2)	0.038(1)	0.027(1)	0.042(1)	0.001(1)	–0.000(1)	–0.001(1)
N(4)	4*e*	–0.0629(2)	0.1554(2)	1.0276(2)	0.038(1)	0.026(1)	0.049(1)	0.002(1)	0.006(1)	0.002(1)
C(1)	4*e*	–0.0149(3)	0.0598(3)	0.9672(2)	0.031(1)	0.026(2)	0.048(2)	–0.001(1)	0.001(1)	0.001(1)
C(2)	4*e*	–0.0891(3)	0.2635(3)	0.9683(3)	0.042(2)	0.026(2)	0.060(2)	0.003(1)	0.005(1)	0.001(1)
C(3)	4*e*	–0.0708(3)	0.2681(3)	0.8501(3)	0.049(2)	0.030(2)	0.056(2)	0.005(1)	0.003(1)	0.011(1)
C(4)	4*e*	–0.0253(3)	0.1644(3)	0.7920(3)	0.037(2)	0.032(2)	0.051(2)	–0.000(1)	0.000(1)	0.005(1)
C(5)	4*e*	–0.1389(4)	0.3749(3)	1.0351(4)	0.089(3)	0.033(2)	0.079(3)	0.015(2)	0.028(2)	0.005(2)
C(6)	4*e*	–0.0122(4)	0.1628(3)	0.6634(3)	0.071(2)	0.052(2)	0.050(2)	0.015(2)	0.002(2)	0.009(2)

References

1. Pointillart, F.; Herson, P.; Boubekeur, K.; Train, C.: Square-planar and trigonal prismatic silver(I) in bipyrimidine and oxalate bridged tetranuclear complexes and one-dimensional compounds: Synthesis and crystal structures. Inorg. Chim. Acta. **361** (2008) 373-379.
2. Morgan, L. W.; Goodwin, K. V.; Pennington, W. T.; Petersen, J. D.: Synthesis and Structure of Infinite-Chain Copper(II) Polymer Systems. Inorg. Chem. **31** (1992) 1103-1106.
3. De Munno, G.; Julve, M.; Verdaguer, M.; Bruno, G.: Bonding Flexibility of 2,2'-Bipyrimidine (*bpm*): Symmetry and Magnetism of Three Copper(II) Complexes with Different Cu:*bpm* Rations. Inorg. Chem. **32** (1993) 2215-2220.
4. De Munno, G.; Julve, M.; Viau, G.; Lloret, F.; Faus, J.; Viterbo, D.: Azido and 2,2'-Bipyrimidine Ligands as Useful Tools in Designing Two- and Three-Dimensional Manganese(II) Networks. Angew. Chem. Int. Ed. **35** (1996) 1807-1810.
5. Julve, M.; De Munno, G.; Bruno, G.; Verdaguer, M.: Synthesis, Structure, and Magnetic Properties of μ-2,2'-Bipyrimidine-*N*,*N*′,*N*″,*N*‴ Copper(II) Complexes. Inorg. Chem. **27** (1988) 3160-3165.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.