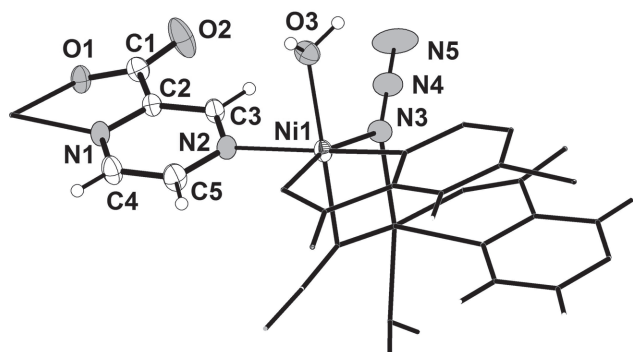


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Crystal structure of two-dimensional coordination polymer *poly*-[μ_2 -azido-aqua-(μ_2 -pyrazine-2-carboxylato- $\kappa^3 O,N:N'$)nickel(II)], $C_5H_5N_5O_3Ni$



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Abstract

$C_5H_5N_5O_3Ni$, monoclinic, $C2/c$ (no. 15), $a = 8.5804(17)$ Å, $b = 13.790(3)$ Å, $c = 13.969(3)$ Å, $\beta = 104.37(3)^\circ$, $V = 1601.2(6)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0203$, $wR_{ref}(F^2) = 0.0550$, $T = 293$ K.

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A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.291 g), pyrazine-2-carboxylic acid (Hpca, 1 mmol, 0.124 g), Et_3N (0.53 mmol, 0.054 g) and NaN_3 (2 mmol, 0.130 g) were mixed in H_2O (10 mL) and heated at 393 K for 2 d in a sealed 25 mL Teflon-lined stainless steel vessel under autogenous pressure. After cooling to room temperature at a rate of $10\text{ K} \cdot \text{h}^{-1}$, green

Table 1: Data collection and handling.

Crystal:	Green block
Size $0.30 \times 0.20 \times 0.20$ mm	
Wavelength:	$Mo\ K\alpha$ radiation (0.71073 Å)
μ :	24.1 cm^{-1}
Diffractometer, scan mode:	Broker APEX-II, ω -scan
$2\theta_{max}$, completeness:	55° , >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	4182, 1563, 0.020
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1510
$N(param)_{refined}$:	136
Programs:	Broker programs [6], SHELX [7]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Ni1	0.19409(2)	0.89293(2)	0.26358(2)	0.01696(10)
O1	0.17710(15)	0.41886(9)	0.34084(9)	0.0229(3)
N1	0.28007(18)	0.54446(11)	0.22830(10)	0.0209(3)
C1	0.1761(2)	0.50641(13)	0.36963(12)	0.0229(4)
O2	0.1343(2)	0.53464(11)	0.44222(11)	0.0451(4)
N2	0.22333(18)	0.74184(11)	0.24324(11)	0.0217(3)
C2	0.2210(2)	0.58026(13)	0.30130(12)	0.0193(3)
O3	0.38316(16)	0.87459(10)	0.38583(10)	0.0262(3)
H31	0.383(4)	0.9017(19)	0.4432(13)	0.065(9)*
H32	0.4798(18)	0.8850(18)	0.376(2)	0.048(8)*
N3	0.02386(19)	0.89273(10)	0.34705(11)	0.0226(3)
C3	0.1960(2)	0.67863(13)	0.30969(13)	0.0220(4)
H3	0.1593	0.7013	0.3629	0.026*
N4	0.02427(19)	0.86781(14)	0.42884(12)	0.0305(4)
C4	0.3082(3)	0.60763(13)	0.16191(14)	0.0279(4)
H4	0.3488	0.5853	0.1101	0.034*
N5	0.0190(3)	0.8420(2)	0.50571(16)	0.0722(8)
C5	0.2782(2)	0.70527(13)	0.16888(13)	0.0278(4)
H5	0.2965	0.7470	0.1205	0.033*

block crystals were isolated. These crystals were washed with methanol and then dried in air, yielding 20%.

Experimental details

H atoms attached to C atoms were placed in geometrically idealized positions (C–H 0.93 Å) and treated as riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The water

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H-atoms were located in a difference Fourier map, and were refined with distance restraint of O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Discussion

The synthesis of paramagnetic metal complexes of high nuclearity and/or spin ground state (S) is currently an active field of research, stimulated to a large extent by the field of molecular magnetism particularly since the discovery of single-molecule magnets (SMMs) in the early 1990s [1]. Homometallic metamagnets have been limitedly documented including metal phosphonates or carboxylates [2] and azido-bridged complexes [3]. In the field of inorganic–organic framework materials, the pyrazinecarboxylate ligand (pca) and its substituted derivatives have proven to be extremely versatile for the synthesis of coordination framework structures due to their ability to engage simultaneously in several different coordination modes [4, 5].

The asymmetric unit of the complex contains one Ni(II), one azido group, one pyrazine-2-carboxylate anion and one coordinated water molecule. The metal atom has a distorted octahedral geometry with two nitrogen atoms from two end-on-coordinated azido groups in *cis*-positions with Ni(1)—N(3) and Ni(1)—N(3B) bond lengths 2.0834 Å and 2.1085 Å, and one oxygen atom of a coordinated water molecule and one carboxylate oxygen atom *trans* to the two azido nitrogen atoms with Ni(1)—O(3) and Ni(1A)—O(1) bond lengths 2.0592 Å and 2.0678 Å respectively. The other two sites are taken up by two aromatic nitrogen atoms from two different pyrazine-2-carboxylate ligands and the bond lengths of Ni(1)—N(2) and Ni(1A)—N(1) are 2.1254 Å and 2.1019 Å respectively. The neighboring metal atoms are connected by two EO-bridging azido ligands. The nearest Ni atoms joined with each other by two $\mu_{1,1}$ -azido forms a 1D

chain which are again joined with each other by the two aromatic nitrogen atoms to give an overall 2-D network.

Atom O3 acts as hydrogen bond donor, *via* H7 to carboxylate O1 and O2 at $(1/2 + x, 1/2 + y, z)$ additionally acts as a hydrogen in the 2D network. O3 bond donor *via* H6 to O2 at $(1/2 - x, 3/2 - y, -z + 1)$, which plays an important role for the interacting between the adjacent two 2D coordination networks.

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