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Crystal structure of poly[bis[μ_3 -1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene- $\kappa^3 N:N':N''$] nickel(II)] hexafluorosilicate, $C_{36}H_{36}N_{12}NiSiF_6$

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Abstract

$C_{36}H_{36}N_{12}NiSiF_6$, trigonal, $P\bar{3}$ (no. 147), $a = 9.5965(3)$ Å, $c = 11.8821(8)$ Å, $V = 947.65(9)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0437$, $wR_{ref}(F^2) = 0.1076$, $T = 223$ 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:	$0.35 \times 0.30 \times 0.25$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.62 mm^{-1}
Diffractometer, scan mode:	Rigaku Mercury,
θ_{max} , completeness:	25.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7417, 1166, 0.047
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1127
$N(\text{param})_{\text{refined}}$:	86
Programs:	CrystalClear [1], SHELX [2, 3]

Source of material

1,3,5-Tris[(1*H*-imidazol-1-yl)methyl]benzene was synthesized according to the method reported previously [4]. All other commercially available chemicals and solvents were of A. R. grade and were used as received without further purification. An amount of 0.2 mmol 1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene, 0.1 mmol nickel sulfate hexahydrate, 0.3 mmol tetrabutylammonium fluoride and 15.0 ml water were mixed and placed in a thick Pyrex tube, which was sealed and heated to 413 K for 96 h. The tube was spontaneously cooled to ambient temperature, where upon green block-shaped crystals were obtained. The presence of Si in the structure results from the reaction of

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ni1	1.0000	1.0000	0.5000	0.0310 (3)
N1	0.8334 (3)	0.7999 (3)	0.40192 (19)	0.0262 (5)
N2	0.6791 (3)	0.6499 (3)	0.26231 (19)	0.0264 (5)
C1	0.7939 (3)	0.7973 (3)	0.2952 (2)	0.0258 (6)
H1A	0.8402	0.8868	0.2483	0.031*
C2	0.7347 (4)	0.6446 (4)	0.4393 (3)	0.0338 (7)
H2A	0.7339	0.6089	0.5122	0.041*
C3	0.6395 (4)	0.5521 (4)	0.3549 (3)	0.0355 (7)
H3A	0.5623	0.4435	0.3587	0.043*
C4	0.6040 (4)	0.6104 (4)	0.1498 (2)	0.0299 (7)
H4A	0.5678	0.4986	0.1326	0.036*
H4B	0.6829	0.6766	0.0936	0.036*
C5	0.4628 (3)	0.6387 (3)	0.1449 (2)	0.0255 (6)
C6	0.3060 (3)	0.5105 (3)	0.1445 (2)	0.0273 (6)
H6A	0.2875	0.4057	0.1440	0.033*
Si1	0.0000	0.0000	0.0000	0.0210 (4)
F1	0.15265 (19)	0.13278 (19)	0.08142 (13)	0.0292 (4)

tetrabutylammonium fluoride with glass. **Elemental analysis:** Calcd. For C₃₆H₃₆N₁₂NiSiF₆: C, 51.58%; H, 4.30%; N, 20.06%; Found: C, 51.16%; H, 4.41%; N, 19.91%.

Experimental details

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93 Å (phenyl & imidazolyl) or 0.97 Å (methylene) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

In the past decades, metal-organic frameworks have attracted much attention because of their fascinating structures and potential applications as functional materials [5–8]. The judicious selection of suitable ligands is vitally important in the construction of new metal-organic frameworks with interesting structures and properties. Imidazole-containing tripodal ligands, for example 1,3,5-tris(1-imidazolyl)benzene [9], 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene [10], 1,3,5-tris(imidazol-1-yl)-2,4,6-trimethylbenzene [11], 1-(1-imidazolyl)-3,5-bis(imidazol-1-ylmethyl)benzene [12], 1,3,5-tris(1*H*-imidazol-1-ylmethyl)-2,4,6-triethylbenzene [13] and 1,3,5-tris[(1*H*-imidazol-1-ylmethyl)benzene(timb) [7], etc., have demonstrated to be powerful building blocks in the assembly of metal-organic frameworks. According to

the previously reported studies, some Ni^{II} complexes with timb, such as *catena*-(bis(μ-1,1',1''-[benzene-1,3,5-triyltris(methylene)]tris(1*H*-imidazole))-(μ-ethane-1,2-diol)-diaqua-disulfato-di-nickel(II) ethane-1,2-diol solvate dihydrate) [14] and *catena*-((μ-1,3,5-tris(imidazol-1-ylmethyl)benzene)-diaqua-(sulfato-*O*)-nickel(II) ethanol solvate monohydrate) [15] have been synthesized and characterized. In the present work, we successfully obtained a new Ni^{II} two-dimensional coordination polymer with timb and Ni(SO₄)·6H₂O via a hydrothermal reaction.

The asymmetric unit consists of one-sixth Ni²⁺ ion, one-third 1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene and one-sixth hexafluorosilicate anion. The Ni²⁺ cation and Si atom are located on a $\bar{3}$ site, the timb molecule only lies on a threefold axis. The coordination sites of Ni(II) are occupied by six N atoms (N1, N1ⁱ, N1ⁱⁱ, N1ⁱⁱⁱ, N1^{iv}, and N1^v) from six different bridging timb ligands [symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $x - y + 1, x, -z + 1$; (iii) $-y + 2, x - y + 1, z$; (iv) $y, -x + y + 1, -z + 1$; (v) $-x + y + 1, -x + 2, z$]. The Ni–N bond length is 2.129(2) Å and the *cis* bond angles around each Ni1 centre in the range 87.11(8)–92.89(8)°. The timb ligand adopts a *cis, cis, cis* substituent conformation and coordinates to three Ni^{II} centres, with equal metal-metal distances of 9.5965(3) Å. The dihedral angles between the least-squares plane of the phenyl moieties and those of the three coordinated imidazole groups are all 75.08(1)°. The three planes of the terminal imidazole ring of the timb ligand are oriented with respect to each other at 66.38(5)°. Each timb ligand links neighboring Ni^{II} centres to form a two-dimensional cationic layered structure extending along the (0 0 1) plane. In the crystal structure of title compound, the Ni^{II} metal complex and SiF₆²⁻ ions are held together by weak intermolecular C–H⋯F hydrogen bonds, resulting in a three-dimensional supramolecular network.

Finally it should be mentioned that structurally directly related Cd(II) complexes have been reported [16].

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