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Crystal structure of diaqua-bis(1,10-phenanthroline $\kappa^2 N, N'$)nickel(II) trifluoroacetate-trifluoroacetic acid (1/1), $C_{30}H_{21}F_9N_4NiO_8$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.29 × 0.22 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.72 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω -scans
$\theta_{\max}$, completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7825, 2789, 0.055
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1773
$N(\text{param})_{\text{refined}}$:	259
Programs:	Bruker programs [1], SHELX [2, 3], OLEX2 [4], DIAMOND [5]

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Abstract

$C_{30}H_{21}F_9N_4NiO_8$, monoclinic, $P2_1/c$ (no. 13), $a = 10.0630(11)$ Å, $b = 9.625(1)$ Å, $c = 18.196(2)$ Å, $\beta = 116.10(3)^\circ$, $V = 1582.7(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0511$, $wR_{\text{ref}}(F^2) = 0.1261$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

All reagents were of analytical grade and used as purchased without further purification. A mixture of nickel oxide

(0.0027 mmol, 0.2049 g), trifluoroacetic acid (HTFA) (0.0054 mol, 0.6140 g) and H₂O (60 mL) were added to the round bottom flask in turn. After refluxing for 2 h, 1,10-phenanthroline (Phen) (0.0014 mmol, 0.2681 g) was added. Continue heating reflux for 6 h, and then the solution was cooled, filtered and recrystallized. Green block-shaped crystals of the title compound were obtained after 3 days.

Experimental details

Absorption corrections were applied by using multi-scan program [1]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were generated geometrically and refined isotropically with a riding model except for those bound to water molecules which were located from the difference Fourier synthesis. Significantly larger ellipsoids for the fluorine atoms of the TFA anions point to a positional disorder.

Comment

The synthesis and applications of fluorinated compounds have recently received significant attention due to their excellent performance in pharmaceuticals, agricultural chemistry and materials science [6–12]. Trifluoromethyl is widely used in the design of drug molecular synthesis because it can significantly improve the metabolic stability, lipophilic property and bioavailability of drug molecules [13–15]. Particularly, the F atom of trifluoroacetic acid can form weak F $\cdots$ F and F $\cdots$ H interactions, which can reinforce the crystal packing and construct more flexible structures. 1,10-Phenanthroline

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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} ^a / <i>U</i> _{eq}
Ni1	0.000000	0.57723(6)	0.250000	0.0480(3)
O1W	0.1279(4)	0.7328(3)	0.2369(2)	0.0606(8)
O1	0.1119(4)	0.1083(4)	0.3130(2)	0.0885(10)
H1A ^a	0.023886	0.114020	0.280980	0.133 [*]
O2	0.0422(3)	−0.0619(3)	0.37090(18)	0.0787(9)
O3	0.3863(3)	0.6494(3)	0.2445(2)	0.0981(12)
N1	−0.1107(4)	0.4271(3)	0.2840(2)	0.0515(8)
N2	0.1397(3)	0.5616(3)	0.37401(19)	0.0522(8)
F1	0.3736(3)	−0.0366(4)	0.4255(2)	0.1435(14)
F2	0.2844(4)	−0.0143(5)	0.5081(2)	0.1569(16)
F3	0.3297(3)	0.1613(3)	0.45731(19)	0.1113(10)
F4 ^a	0.3993(18)	0.9190(10)	0.2599(16)	0.165(6)
F5 ^a	0.6276(15)	0.9073(11)	0.3027(9)	0.142(4)
H1WA	0.084(4)	0.800(4)	0.210(2)	0.053(13) [*]
H1WB	0.223(7)	0.720(5)	0.242(3)	0.14(2) [*]
F6 ^a	0.490(2)	0.8949(14)	0.1755(8)	0.236(6)
C1	−0.2357(5)	0.3615(4)	0.2387(3)	0.0642(11)
H1	−0.287219	0.386553	0.183916	0.077 [*]
C2	−0.2940(6)	0.2573(4)	0.2685(4)	0.0816(15)
H2	−0.381973	0.213276	0.234370	0.098 [*]
C3	−0.2208(6)	0.2210(4)	0.3480(4)	0.0795(15)
H3	−0.258298	0.150944	0.368796	0.095 [*]
C4	−0.0880(5)	0.2883(4)	0.3999(3)	0.0638(12)
C5	−0.0384(5)	0.3902(4)	0.3635(3)	0.0541(10)
C6	0.0966(5)	0.4634(4)	0.4123(3)	0.0544(10)
C7	0.1772(5)	0.4319(4)	0.4957(3)	0.0629(11)
C8	0.1214(6)	0.3271(5)	0.5298(3)	0.0794(14)
H8	0.173133	0.305640	0.585088	0.095 [*]
C9	−0.0034(7)	0.2591(5)	0.4844(4)	0.0813(15)
H9	−0.035864	0.190554	0.508684	0.098 [*]
C10	0.3063(6)	0.5063(5)	0.5395(3)	0.0759(13)
H10	0.363176	0.488102	0.594868	0.091 [*]
C11	0.3497(5)	0.6057(5)	0.5016(3)	0.0724(12)
H11	0.435571	0.656628	0.530729	0.087 [*]
C12	0.2643(5)	0.6303(4)	0.4189(3)	0.0618(11)
H12	0.295560	0.698035	0.393497	0.074 [*]
C13	0.1280(5)	0.0243(4)	0.3693(3)	0.0608(11)
C14	0.2773(5)	0.0352(5)	0.4412(3)	0.0732(13)
C15	0.500000	0.7027(6)	0.250000	0.0568(15)
C16	0.500000	0.8594(7)	0.250000	0.088(2)

^aOccupancy: 0.5.

is a multidentate ligand with a rigid structure, which may adopt diverse binding modes to construct novel functional complexes [16]. However, as far as we know, trifluoroacetic coordination compounds, especially compounds with strong hydrogen bonding interactions between transition metal complexes and guest molecules are rarely reported.

The basic structural unit of the title compound [Ni(Phen)₂(H₂O)₂] (TFA)₂·HTFA consists of one diaquabis(1,10-phenanthroline) with nickel [Ni(Phen)₂(H₂O)₂]²⁺ cation, two trifluoroacetate anions and one independent

trifluoroacetic acid molecule (see the figure). The central Ni ion exhibits a distorted octahedral coordination, defined by four nitrogen atoms from two different Phen ligands and two oxygen atoms from two individual water molecules. The HTFA molecule and TFA anions remain uncoordinated. The Ni–O bond length is 2.055(3) Å, and two Ni–N bond lengths are 2.073(3) and 2.079(3) Å. The N–Ni–N bite angles are all 79.67(13)°. The angle of OW–Ni–OW is 86.48(18)°. The bond angles of OW–Ni–N are in the range of 91.13(12)° and 170.41(13)°. The fluorine atoms of the TFA anions of the HTFA molecule of the title compound are disordered over two positions. The water molecules in the structure of the title compound participate in the formation of intermolecular hydrogen bonds: (a) hydrogen bonds (O1W–H1WB···O3: 2.666(4) Å and 165(5)°) with TFA anions, which connect the mononuclear units to form a chain structure along the *a* axis; (b) hydrogen bonds (O1W–H1WA···O2³: 2.780(4) Å and 170(4)°: *−x*, *y* + 1, *−z* + 1/2) link the uncoordinated HTFA molecule. Furthermore, there are intermolecular hydrogen bonds between adjacent HTFA molecules (O1–H1A···O1¹: 2.404(7) Å and 151.0°: *−x*, *+**y*, 1/2 *−z*). The molecular structure and packing are stabilized by intermolecular O–H···O hydrogen bond interactions. Geometric parameters are within the expectations [17].

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