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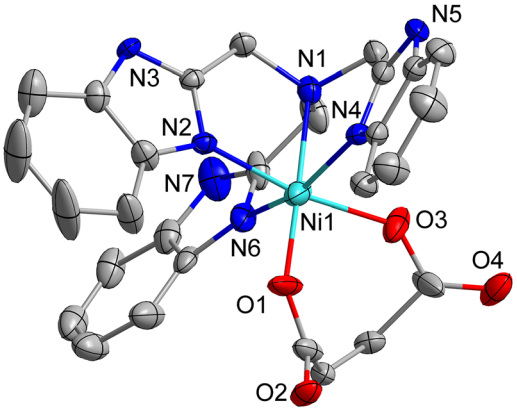
Crystal structure of {tris((1*H*-benzo[*d*]imidazol-2-yl)methyl)amine-κ^4N,N',N'',N'''}-(succinato-κ^2O,O')nickel(II) – methanol (1/4), $C_{32}H_{41}N_7NiO_8$



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Abstract

$C_{32}H_{41}N_7NiO_8$, monoclinic, $P2_1/c$ (no. 14), a = 10.0076(5) Å, b = 18.6561(10) Å, c = 19.0893(18) Å, β = 108.532(6)°, V = 3378.4(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0607, $wR_{ref}(F^2)$ = 0.1340, T = 111.9(1) K.

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The molecular structure is shown in the figure (four solvent molecules which belong to the asymmetric unit are not shown). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tris(benzimidazol-2-yl-methyl)amine (ntb) was synthesized according to a literature procedure [4]. A methanol solution (50 mL) of $Ni(ClO_4)_2{\cdot}6H_2O$ (73 mg, 0.2 mmol) and ntb (82 mg, 0.2 mmol) was stirred for 10 min. Then a methanol solution (40 mL) of disodium succinate hexahydrate (54 mg, 0.2 mmol) was added dropwise to the aforementioned solution. After being stirred at room temperature for 2 h, the solution was filtered for slow evaporation. Light-blue crystals formed.

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.34 × 0.32 × 0.30 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.64 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	26.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16175, 6632, 0.055
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4640
$N(param)_{refined}$:	448
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3]

Experimental details

The structure was solved with the Olex2 program [2]. The methyl groups were idealized and refined using rigid groups allowed to rotate about the N–C bond (with the SHELX program [3]). The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 U_{eq} and the values of all other hydrogen atoms were set to 1.2 U_{eq}. The disordered C27 and C28 atoms of succinate including H atoms on them were located at two sites with occupancies to be 0.503(5) for C27, C28 and 0.497(5) for C27′, C28′ (Table 2).

Comment

The ligand ntb is often used in the construction of a variety of metal complexes [5]. Some mononuclear nickel(II) complexes have been reported which use monocarboxylate (isonicotinate, picolinate and 3, 5-dinitrobenzoate), azide

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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}
C1	−0.2079 (3)	0.35410 (19)	0.13583 (18)	0.0209 (7)
H1A	−0.273228	0.395496	0.124452	0.025*
H1B	−0.265262	0.309762	0.125465	0.025*
C2	−0.1232 (3)	0.35589 (17)	0.21544 (18)	0.0156 (7)
C3	0.0529 (4)	0.35991 (18)	0.31572 (19)	0.0225 (8)
C4	−0.0697 (4)	0.35832 (18)	0.33607 (19)	0.0223 (8)
C5	−0.0652 (5)	0.3596 (2)	0.4096 (2)	0.0378 (10)
H5A	−0.148847	0.358306	0.422916	0.045*
C6	0.0653 (5)	0.3629 (3)	0.4619 (2)	0.0605 (15)
H6	0.072830	0.363675	0.512809	0.073*
C7	0.1876 (5)	0.3651 (3)	0.4415 (2)	0.0640 (16)
H7A	0.276241	0.367728	0.479218	0.077*
C8	0.1849 (4)	0.3636 (2)	0.3690 (2)	0.0385 (11)
H8	0.269026	0.364986	0.356023	0.046*
C9	−0.1369 (4)	0.42405 (18)	0.04423 (19)	0.0233 (8)
H9A	−0.236349	0.439825	0.030601	0.028*
H9B	−0.112959	0.416519	−0.001719	0.028*
C10	−0.0420 (4)	0.47997 (18)	0.09122 (19)	0.0216 (8)
C11	0.1407 (3)	0.52716 (18)	0.17066 (19)	0.0205 (8)
C12	0.0514 (4)	0.58354 (18)	0.1359 (2)	0.0220 (8)
C13	0.0850 (4)	0.65469 (19)	0.1541 (2)	0.0287 (9)
H13	0.023488	0.692540	0.130617	0.034*
C14	0.2115 (4)	0.6679 (2)	0.2079 (2)	0.0367 (10)
H14	0.238549	0.716000	0.221546	0.044*
C15	0.3014 (4)	0.6119 (2)	0.2430 (2)	0.0338 (9)
H15	0.388310	0.623173	0.279604	0.041*
C16	0.2673 (4)	0.54087 (19)	0.2258 (2)	0.0261 (8)
H16	0.327635	0.503115	0.250581	0.031*
C17	−0.1357 (4)	0.29061 (19)	0.0414 (2)	0.0321 (9)
H17A	−0.094032	0.297107	0.001200	0.039*
H17B	−0.236986	0.279055	0.019120	0.039*
C18	−0.0617 (4)	0.23234 (19)	0.0923 (2)	0.0279 (9)
C19	0.0899 (4)	0.18070 (18)	0.1843 (2)	0.0243 (8)
C20	−0.0109 (4)	0.12876 (19)	0.1504 (2)	0.0280 (9)
C21	−0.0043 (4)	0.05951 (19)	0.1778 (2)	0.0314 (9)
H21	−0.072449	0.024329	0.154316	0.038*
C22	0.1054 (4)	0.0443 (2)	0.2404 (2)	0.0359 (10)
H22	0.113444	−0.002661	0.260660	0.043*
C23	0.2057 (4)	0.0961 (2)	0.2753 (3)	0.0382 (10)
H23	0.279570	0.083534	0.318870	0.046*
C24	0.2001 (4)	0.1647 (2)	0.2480 (2)	0.0356 (10)
H24	0.268694	0.199605	0.271730	0.043*
C25	0.4248 (4)	0.33511 (18)	0.2196 (2)	0.0246 (8)
C26	0.2643 (5)	0.3365 (2)	0.0444 (2)	0.0411 (11)
C27[a]	0.4526 (10)	0.2907 (5)	0.1503 (5)	0.0196 (14)
H27A[a]	0.509596	0.321924	0.128771	0.024*
H27B[a]	0.511185	0.248353	0.171320	0.024*
C27′[b]	0.4153 (10)	0.2781 (5)	0.1700 (5)	0.0196 (14)
H27C[b]	0.327782	0.250541	0.163723	0.024*
H27D[b]	0.496597	0.245384	0.189502	0.024*
C28[a]	0.3269 (7)	0.2649 (4)	0.0875 (4)	0.0204 (11)
H28A[a]	0.257068	0.241001	0.106518	0.024*
H28B[a]	0.356324	0.231049	0.055197	0.024*
C28′[b]	0.4148 (7)	0.3092 (4)	0.0950 (4)	0.0204 (11)
H28C[b]	0.448615	0.271925	0.067790	0.024*
H28D[b]	0.482006	0.349771	0.104165	0.024*
C29	0.6529 (5)	0.5039 (2)	0.3587 (2)	0.0454 (11)
H29A	0.599986	0.532994	0.316275	0.068*
H29B	0.732629	0.480966	0.348218	0.068*
H29C	0.688129	0.534561	0.402420	0.068*
C30	0.5114 (5)	0.2784 (4)	−0.0970 (3)	0.0788 (19)
H30A	0.505314	0.307451	−0.140611	0.118*
H30B	0.422805	0.252236	−0.105007	0.118*
H30C	0.589201	0.244113	−0.088428	0.118*
C31	−0.4254 (7)	0.0810 (6)	0.0464 (4)	0.173 (5)
H31A	−0.515824	0.062527	0.014271	0.259*
H31B	−0.442210	0.118898	0.078069	0.259*
H31C	−0.372033	0.041951	0.077159	0.259*
C32	0.4594 (4)	0.4982 (3)	0.1160 (2)	0.0477 (12)
H32A	0.366858	0.475068	0.097356	0.072*
H32B	0.447573	0.550377	0.112812	0.072*
H32C	0.504937	0.484324	0.167646	0.072*
N1	−0.1174 (3)	0.35652 (14)	0.08711 (15)	0.0203 (6)
N2	0.0154 (3)	0.35792 (14)	0.23932 (14)	0.0165 (6)
N3	−0.1805 (3)	0.35595 (14)	0.27041 (15)	0.0183 (6)
H3	−0.270865	0.354720	0.265559	0.022*
N4	0.0787 (3)	0.46250 (15)	0.14095 (15)	0.0193 (6)
N5	−0.0646 (3)	0.55125 (15)	0.08568 (15)	0.0217 (7)
H5	−0.138937	0.573146	0.055888	0.026*
N6	0.0550 (3)	0.24494 (15)	0.14593 (17)	0.0245 (7)
N7	−0.1068 (4)	0.16396 (16)	0.09182 (17)	0.0336 (8)
H7	−0.182998	0.145281	0.060194	0.040*
Ni1	0.10551 (5)	0.35324 (2)	0.15663 (3)	0.02142 (14)
O1	0.3085 (2)	0.35461 (14)	0.22464 (16)	0.0396 (7)
O2	0.5401 (2)	0.35651 (13)	0.26313 (12)	0.0253 (6)
O3	0.1566 (3)	0.35167 (13)	0.05988 (15)	0.0345 (7)
O4	0.2918 (3)	0.36258 (15)	−0.00957 (14)	0.0347 (7)
O5	0.5632 (3)	0.45025 (15)	0.37227 (14)	0.0376 (7)
H5B	0.543087	0.420215	0.337695	0.056*
O6	0.5354 (4)	0.3229 (4)	−0.0354 (3)	0.148 (3)
H6A	0.457870	0.335828	−0.031219	0.222*
O7	−0.3525 (5)	0.1073 (2)	0.00527 (18)	0.0793 (13)
H7B	−0.383861	0.090430	−0.037661	0.119*
O8	0.5417 (4)	0.4769 (3)	0.0743 (3)	0.118 (2)
H8A	0.492191	0.453989	0.037272	0.178*

[a]Occupancy: 0.497(5), [b]Occupancy: 0.503(5).

and 2-(2′-pyridyl)-4, 4, 5, 5-tetramethylimidazoline-1-oxyl-3-oxide (NIT2Py) [6–8] as coligands, respectively. Two dinuclear nickel(II) complexes of ntb were prepared and characterized using dicarboxylate (terephthalate and fumarate) as bridging ligands by our group [9]. Succinic acid is a saturated aliphatic dicarboxylic acid. It shows conformational freedom and coordination versatility due to the single-bonded carbon chains, coordinating metal ions in various modes [10–13]. As an extension of our work, succinate was selected for the construction of a nickel(II) complex

of ntb. At this time, the effort to get a dinickel(II) complex failed, while a mononuclear complex was obtained.

The title complex was obtained by the reaction of $Ni(ClO_4)_2{\cdot}6H_2O$, ntb and disodium succinate hexahydrate in the ratio of 2:2:1 in methanol. The asymmetric unit of the title structure consists of one [Ni(ntb)(suc)] unit and four methanol molecules. The central Ni(II) is six-coordinate in a N_4O_2 donor set formed by four nitrogen atoms of ntb and two oxygen atoms of succinate. The equatorial plane is defined by N2, N4, N6 of ntb and O3 of succinate. Equatorial bond angles are in the range 86.68(10)–91.14(11)°. The apical positions are occupied by O1 of succinate and tertiary amine N1 of ntb with O1–Ni1–N1 bond angle to be 176.64°, showing a distorted octahedral environment. As expected, the tripodal ntb ligand coordinates nickel(II) with the three benzimidazole groups in a T-shaped fashion. This can be observed almost in all nickel(II) complexes of ntb [7–9, 14, 15]. The three benzimidazole Ni–N bond lengths are in the range of 2.054(3)–2.077(3) Å, while the Ni–N(tertiary amine) bond length is 2.205(3) Å. The succinate anion shows a bidentate chelating mode. Each carboxylate provides one oxygen atom (O1, O3) to coordinate with nickel(II) to form a seven-membered ring. The two Ni–O bond lengths are 2.033(3) Å for Ni1–O1 and 2.067(2) Å for Ni1–O3, respectively. The O1–Ni–O3 bond angle is 95.16(11)°. This coordination is different to previously reported dicarboxylato-nickel(II) complexes of ntb. In the complexes $[Ni_2(ntb)_2(\mu\text{-tp})(H_2O)_2](NO_3)_2{\cdot}4CH_3OH{\cdot}H_2O$ and $[Ni_2(ntb)_2(\mu\text{-fum})(H_2O)(CH_3OH)](NO_3)_2{\cdot}6CH_3OH{\cdot}H_2O$, two $[Ni(ntb)]^{2+}$ units are bridged by terephthalate and fumarate in bis(monodentate) mode [7]. Thus, we showed that the single-bonded carbon chain of succinate is flexible enough to adopt the bidentate chelating mode.

In the complex, two of the [Ni(ntb)(suc)] units are interlinked by H-bonds to form a dimolecular unit [N5–H5⋯O4, d(D⋯A) = 2.786(4) Å]. These dimolecular units are interacted to form a chain structure by H-bonds through the carboxylate (O2) of succinate and the benzimidazole NH(N3) groups of ntb [N3–H3⋯O2, d(D⋯A) = 2.756(3) Å]. The chains are further expanded into a 2D network structure by weak π-π interaction between benzimidazole groups.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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