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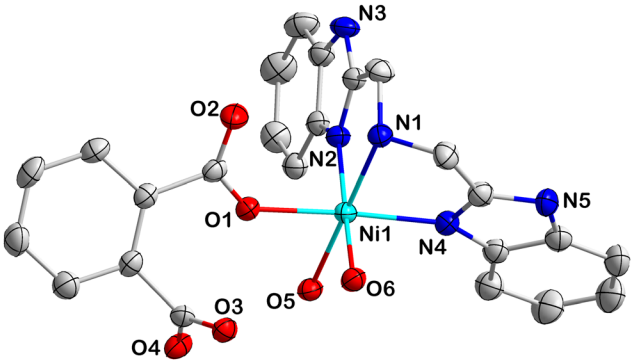
Crystal structure of diaqua[bis(benzimidazol-2-yl-methyl)amine-κ^3*N*,*N*′,*N*″]-phthalato-κ^1*O*-nickel(II)-methanol (1/2), $C_{26}H_{31}N_5NiO_8$



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Abstract

$C_{26}H_{31}N_5NiO_8$, monoclinic, $P2_1/n$ (no. 14), a = 12.554(3) Å, b = 12.401(3) Å, c = 18.718(5) Å, β = 107.844(3)°, V = 2774.0(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0438, $wR_{ref}(F^2)$ = 0.1175, T = 153(2) K.

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The molecular structure is shown in the Figure. 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:	Blue platelet
Size:	0.27 × 0.20 × 0.07 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.76 mm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ and ω
θ_{max}, completeness:	29.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30,130, 7431, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 5655
$N(param)_{refined}$:	367
Programs:	CrystalClear [1], Olex2 [2], SHELX [3]

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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}
Ni1	0.68986 (2)	0.37074 (2)	0.63642 (2)	0.02025 (8)
O1	0.60208 (11)	0.46465 (10)	0.68755 (8)	0.0242 (3)
O2	0.58483 (14)	0.37088 (11)	0.78566 (9)	0.0352 (4)
O3	0.38114 (11)	0.49603 (10)	0.57335 (8)	0.0253 (3)
O4	0.47766 (12)	0.64950 (11)	0.58275 (8)	0.0281 (3)
O5	0.69125 (11)	0.51436 (10)	0.57738 (8)	0.0244 (3)
H5A	0.6709	0.5067	0.5305	0.029*
H5B	0.6421	0.5514	0.5880	0.029*
O6	0.53143 (11)	0.33192 (11)	0.56231 (8)	0.0251 (3)
H6A	0.4799	0.3695	0.5694	0.030*
H6B	0.5329	0.3387	0.5180	0.030*
N1	0.68523 (15)	0.22587 (13)	0.69600 (9)	0.0240 (3)
N2	0.83695 (13)	0.39126 (13)	0.71896 (9)	0.0225 (3)
N3	0.95186 (14)	0.33110 (14)	0.82708 (10)	0.0289 (4)
H3	0.9794	0.2890	0.8662	0.035*
N4	0.75799 (13)	0.26538 (13)	0.57688 (9)	0.0243 (3)
N5	0.77184 (14)	0.09276 (14)	0.54784 (10)	0.0282 (4)
H5	0.7630	0.0223	0.5474	0.034*
C1	0.78455 (18)	0.21748 (16)	0.76292(12)	0.0297 (4)
H1A	0.8273	0.1517	0.7593	0.036*
H1B	0.7605	0.2114	0.8084	0.036*
C2	0.85745 (16)	0.31381 (16)	0.76929 (11)	0.0239 (4)
C3	0.99677 (16)	0.42765 (17)	0.81280 (12)	0.0275 (4)
C4	1.09036 (18)	0.48612 (19)	0.85326 (13)	0.0364 (5)
H4	1.1391	0.4607	0.8997	0.044*
C5	1.10900 (18)	0.5833 (2)	0.82250 (14)	0.0396 (5)
H5C	1.1716	0.6260	0.8487	0.048*
C6	1.03829 (18)	0.61984 (17)	0.75413 (14)	0.0330 (5)
H6	1.0545	0.6865	0.7347	0.040*
C7	0.94485 (16)	0.56188 (16)	0.71352 (12)	0.0259 (4)
H7	0.8970	0.5873	0.6668	0.031*
C8	0.92440 (16)	0.46498 (16)	0.74421 (11)	0.0235 (4)
C9	0.67222 (18)	0.13598 (15)	0.64262 (12)	0.0288 (4)
H9A	0.5920	0.1243	0.6154	0.035*
H9B	0.7030	0.0688	0.6697	0.035*
C10	0.73431 (16)	0.16454 (16)	0.58837 (12)	0.0262 (4)
C11	0.82695 (17)	0.15094 (17)	0.50695 (12)	0.0289 (4)
C12	0.88330 (19)	0.11935 (19)	0.45696 (14)	0.0384 (5)
H12	0.8880	0.0458	0.4442	0.046*
C13	0.9318 (2)	0.1996 (2)	0.42700 (15)	0.0435 (6)
H13	0.9705	0.1813	0.3923	0.052*
C14	0.9254 (2)	0.3081 (2)	0.44658 (14)	0.0414 (6)
H14	0.9613	0.3613	0.4256	0.050*
C15	0.86820 (18)	0.33948 (19)	0.49548 (13)	0.0331 (5)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H15	0.8631	0.4132	0.5079	0.040*
C16	0.81872 (16)	0.25922 (16)	0.52546 (11)	0.0264 (4)
C17	0.56180 (16)	0.44839 (15)	0.74095 (11)	0.0237 (4)
C18	0.48024 (16)	0.53347 (15)	0.74865 (11)	0.0229 (4)
C19	0.46838 (17)	0.55502 (17)	0.81888 (12)	0.0297 (4)
H19	0.5088	0.5133	0.8610	0.036*
C20	0.3985 (2)	0.63636 (18)	0.82780 (13)	0.0363 (5)
H20	0.3924	0.6516	0.8761	0.044*
C21	0.33760 (19)	0.69563 (19)	0.76646 (14)	0.0365 (5)
H21	0.2876	0.7499	0.7724	0.044*
C22	0.34905 (17)	0.67629 (18)	0.69661 (13)	0.0317 (5)
H22	0.3079	0.7182	0.6547	0.038*
C23	0.42075 (15)	0.59551 (16)	0.68732 (11)	0.0238 (4)
C24	0.42846 (15)	0.57785 (16)	0.60915 (11)	0.0233 (4)
O7	0.73283 (18)	0.37878 (13)	0.92406 (11)	0.0581 (6)
H7A	0.6793	0.3672	0.8850	0.070*
O8	0.2412 (2)	0.35778 (16)	0.62579 (15)	0.0708 (7)
H8	0.2874	0.3951	0.6122	0.085*
C25	0.7492 (3)	0.2887 (2)	0.97078 (17)	0.0705 (9)
H25A	0.8282	0.2841	1.0007	0.085*
H25B	0.7279	0.2234	0.9402	0.085*
H25C	0.7029	0.2952	1.0043	0.085*
C26	0.1577 (3)	0.4251 (3)	0.6369 (3)	0.0983 (15)
H26A	0.1082	0.3828	0.6577	0.118*
H26B	0.1140	0.4566	0.5889	0.118*
H26C	0.1926	0.4829	0.6720	0.118*
H1	0.6267 (19)	0.2290 (17)	0.7133 (13)	0.029 (6)*

Source of material

Bis(benzimidazol-2-yl-methyl)amine (bbma) was synthesized according to a literature procedure [4]. A methanol solution (25 ml) of $Ni(NO_3)_2{\cdot}6H_2O$ (58 mg, 0.2 mmol) and bbma (55 mg 0.2 mmol) was mixed. Then a methanol solution (20 ml) of phthalic acid (33 mg, 0.2 mmol) and triethylamine (40 mg, 0.4 mmol) was dropped to the above solution. After being stirred at room temperature for 5 h, the solution was filtered for slow evaporation. Light blue crystals formed.

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 C–O bond (with the SHELX program [3]). The U_{iso} values of all the hydrogen atoms were set to 1.2 U_{eq}.

Comment

Phthalate (pht) is a versatile ligand which adopts many coordination modes due to a variety of its bonding abilities [5–8]. It is used in the design of coordination compounds. Bis(benzimidazol-2-yl-methyl)amine (bbma) is a tridentate ligand with two benzimidazole groups attached to a nitrogen atom. This ligand is often used to prepare metal complexes in the use of modeling the active sites of relevant metalloenzymes. Compared to other metal complexes, nickel(II) complexes of bbma are rare. Several nickel(II) complexes with bis(bbma) have been structurally characterized [9]. To the best of our knowledge, only three nickel(II) complexes of bbma containing picolinate, thiocyanate and dicyandiamide as coligands have been reported [10–12].

The title compound consists of a neutral $[Ni(bbma)(pht)(H_2O)_2]$ and two methanol molecules. The Ni(II) atom is coordinated by three nitrogen atoms (N1, N2, N4) of bbma, one carboxylate oxygen atom (O1) of phthalate and two oxygen atoms (O5, O6) of water molecules, adopting a distorted octahedral geometry (see the Figure). The equatorial plane of Ni(II) is constructed by N2, N4, O1, O6 with the bond angles from 84.38(6)° to 93.89(6)°. The axial positions are occupied by N1 and O5 with bond angle of 178.92(6)°. The phthalate coordinates to nickel(II) by one of its carboxylate groups in an unidentate way, with the bond length of 2.0331(13) Å, which is shorter than $Ni–O_{water}$=2.0990(14) Å for Ni1–O5 and 2.1026(14) Å for Ni1–O6. In this complex, bbma behaves as a tridentate ligand, where the three Ni–N distances are ranging from 2.0281(17) Å to 2.1248(17) Å, with the $Ni–N_{alkylamine}$ significantly longer than the $Ni–N_{benzimidzole}$. The most striking feature is that two benzimidazole groups of bbma are not coplanar. They are bent with a dihedral angle of 98.18°. This is quite different from the reported copper(II) complex $[Cu(bbma)(pht)]CH_3OH{\cdot}2H_2O$, in which the two benzimidazole groups of bbma are nearly coplanar with the dihedral angel to be 170.72° [13]. The copper(II) is coordinated in a distorted square pyramidal geometry with τ value of 0.19. Phthalate coordinates to the central copper(II) ion through only one of its carboxylate groups in bidentate cheating way.

In this complex, hydrogen bonding interactions play an important role in the crystal packing, while no π–π interactions between the aromatic rings were observed. Two intramolecular hydrogen bonding interactions can be observed between the NH(N1) of bbma and the carboxylate group O2 of phthalate, and between the uncoordinated carboxylate O3 atom and O6 (coordinated water molecule). Two neighbouring molecules are linked by O–H···O intermolecular hydrogen bonds to form a dinuclear unit,

involving the uncoordinated carboxylate group (O3, O4) of phathlate and two coordinating aqua molecules (O5, O6). These dinuclear units are hydrogen bonded by the NH(N3) group of bbma and O4 to form a 1D chain structure. The 1D chain are further expanded into 2D network structure involving the NH(N5) group of bbma, methanol molecule (O7) and O2 through N–H···O and O–H···O hydrogen bonds.

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

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