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Crystal structure of diaqua-bis(3-carboxy-5-bromoisophthalato- κO)-bis(1-(3-(1*H*-benzo[d]imidazol-1-yl)propyl)-1*H*-benzo[d]imidazol-3-ium- κN) nickel(II) bis(3-carboxy-5-bromoisophthalate), $C_{66}H_{54}Br_4N_8NiO_{18}$

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Abstract

$C_{66}H_{54}Br_4N_8NiO_{18}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.821(2)$ Å, $b = 14.6587(14)$ Å, $c = 14.8211(14)$ Å, $\alpha = 119.608(1)^\circ$, $\beta = 95.365(1)^\circ$, $\gamma = 99.249(1)^\circ$, $V = 1610.8(5)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0345$, $wR_{ref}(F^2) = 0.0815$, $T = 296(2)$ K.

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A part 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 material

5-Bromoisophthalic acid (Brip, 24.5 mg, 0.1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (24.7 mg, 0.1 mmol), and 1,3-bis(benzimidazol-1-yl)propane (bbp, 27.6 mg, 0.1 mmol) were added to water (9 mL) in a 25 mL Teflon-lined autoclave. The mixture was heated at 413 K for 3 days and then slowly cooled to room temperature. Green block crystals were obtained.

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Table 1: Data collection and handling.

Crystal:	Block, clear light green
Size:	$0.24 \times 0.21 \times 0.16$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.86 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12096, 5952, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4696
$N(\text{param})_{\text{refined}}$:	447
Programs:	Bruker programs [1], SHELX [2, 3]

Experimental details

The hydrogen atoms were placed in calculated positions riding on attached atoms with isotropic thermal parameters.

Discussion

In the last two decades, a large number of supramolecular assemblies using the derivatives of isophthalic acid (H_2ip) as functional groups have been reported in the literature [4–8]. However it is still anticipated that modifications at the 5-position may afford different supramolecular network in view of their electronic effect. In addition, the flexible ligands with N-donor co-ligands have been widely utilized in the construction of supramolecule. Among N-donor ligand, 1,3-bis(benzimidazol-1-yl)propane (bbp), not only can act as bidentate ligand to coordinate to two metal ions [9–11], but also act as monodentate ligand to coordinate to one metal ions and another N atom can be protonated and acts as hydrogen bonding donor [12].

In the title complex, there are one half $Ni(II)$ ion, one coordinated HBrip ligand, one Hbbp and one coordinated water molecules as well as one free HBrip anion in the asymmetric unit (Figure top). Ni1 is six-coordinated with a distorted octahedral geometry by two O atoms from two HBrip and a pair of N atoms of two bia ligands, located at the basal equatorial plane, and two coordinated water molecules from the axial positions with a $O9-Ni1-O9'$ angle of 180° . The $Ni-N$ bond lengths are $2.078(2)$ Å and the $Ni-O$ ones are $2.0667(17)$ and $2.1097(19)$ Å. In the title complex, there are three kinds of hydrogen bonds: (a) intramolecular hydrogen bonding between coordinated water and carboxylate O atoms of coordinated HBrip with $d(O \cdots O) = 2.73$ Å;

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.5000	0.5000	0.01879(11)
Br1	0.21628(5)	−0.08212(3)	0.48928(3)	0.05615(13)
Br2	0.83531(6)	0.35946(3)	−0.21832(3)	0.07051(15)
O1	0.4208(2)	0.33964(13)	0.45357(14)	0.0241(4)
O2	0.4037(2)	0.34876(15)	0.60684(15)	0.0345(5)
O3	0.4842(3)	−0.13522(16)	0.16131(18)	0.0485(6)
H3	0.5205	−0.1562	0.1074	0.073*
O4	0.5511(3)	0.02395(16)	0.17278(17)	0.0439(6)
O5	0.6002(3)	0.80249(16)	−0.00745(16)	0.0411(5)
O6	0.6833(2)	0.72421(15)	−0.15767(15)	0.0344(5)
O7	0.6486(4)	0.66136(19)	0.22881(18)	0.0587(7)
H7A	0.6273	0.6570	0.2795	0.088*
O8	0.6868(3)	0.49615(19)	0.17172(19)	0.0515(6)
O9	0.5448(2)	0.44261(17)	0.34600(15)	0.0272(4)
H9A	0.555(4)	0.497(3)	0.342(3)	0.041*
H9B	0.483(4)	0.400(3)	0.298(3)	0.041*
N1	0.2722(2)	0.50215(17)	0.45223(17)	0.0232(5)
N2	0.0443(2)	0.45307(17)	0.34232(16)	0.0238(5)
N3	−0.2107(3)	0.11047(18)	0.00990(18)	0.0302(5)
N4	−0.2281(3)	−0.06227(19)	−0.08787(19)	0.0334(6)
H4	−0.2529	−0.1304	−0.1111	0.040*
C1	0.4040(3)	0.2979(2)	0.5095(2)	0.0232(6)
C2	0.3847(3)	0.1765(2)	0.4524(2)	0.0243(6)
C3	0.4320(3)	0.1251(2)	0.3564(2)	0.0248(6)
H3A	0.4671	0.1648	0.3260	0.030*
C4	0.4279(3)	0.0156(2)	0.3048(2)	0.0267(6)
C5	0.3653(3)	−0.0459(2)	0.3456	0.0322(7)
H5	0.3599	−0.1197	0.3111	0.039*
C6	0.3114(4)	0.0049(2)	0.4386(2)	0.0335(7)
C7	0.3233(3)	0.1152(2)	0.4943(2)	0.0303(6)
H7	0.2910	0.1479	0.5587	0.036*
C8	0.4946(3)	−0.0308(2)	0.2067(2)	0.0296(6)
C9	0.6510(3)	0.7278(2)	−0.0747(2)	0.0276(6)
C10	0.6820(3)	0.6398(2)	−0.0559(2)	0.0265(6)
C11	0.7328(4)	0.5540(2)	−0.1322(2)	0.0331(7)
H11	0.7445	0.5495	−0.1959	0.040*
C12	0.7659(4)	0.4755(2)	−0.1126(3)	0.0387(7)
C13	0.7491(4)	0.4802(3)	−0.0192(3)	0.0402(8)
H13	0.7714	0.4267	−0.0073	0.048*
C14	0.6984(3)	0.5659(2)	0.0572(2)	0.0334(7)
C15	0.6642(3)	0.6451(2)	0.0384(2)	0.0301(6)
H15	0.6292	0.7020	0.0894	0.036*
C16	0.6784(4)	0.5699(3)	0.1582(3)	0.0380(7)
C18	0.1978(3)	0.5874(2)	0.4923(2)	0.0222(6)
C19	0.2422(3)	0.6886(2)	0.5843(2)	0.0272(6)
H19	0.3338	0.7085	0.6330	0.033*
C20	0.1457(3)	0.7586(2)	0.6011(2)	0.0306(7)
H20	0.1743	0.8275	0.6614	0.037*
C21	0.0061(3)	0.7283(2)	0.5295(2)	0.0325(7)
H21	−0.0554	0.7779	0.5429	0.039*
C22	−0.0428(3)	0.6274(2)	0.4399(2)	0.0278(6)
H22	−0.1368	0.6068	0.3931	0.033*
C23	0.0559(3)	0.5574(2)	0.4227(2)	0.0232(6)
C24	0.1755(3)	0.4251(2)	0.3642(2)	0.0243(6)
H24	0.1956	0.3579	0.3212	0.029*
C25	−0.0885(3)	0.3914(2)	0.2526(2)	0.0302(6)

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H25A	−0.0933	0.4277	0.2130	0.036*
H25B	−0.1847	0.3901	0.2792	0.036*
C26	−0.0784(3)	0.2766(2)	0.1787(2)	0.0301(6)
H26A	−0.0629	0.2417	0.2188	0.036*
H26B	0.0104	0.2769	0.1449	0.036*
C27	−0.2281(3)	0.2146(2)	0.0952(2)	0.0334(7)
H27A	−0.3131	0.2021	0.1278	0.040*
H27B	−0.2548	0.2573	0.0656	0.040*
C28	−0.2682(3)	0.0136(2)	−0.0042(2)	0.0332(7)
H28	−0.3281	0.0011	0.0388	0.040*
C29	−0.1280(3)	0.0966(2)	−0.0697(2)	0.0291(6)
C30	−0.1396(3)	−0.0138(2)	−0.1319(2)	0.0293(6)
C31	−0.0724(4)	−0.0564(3)	−0.2209(2)	0.0382(7)
H31	−0.0794	−0.1301	−0.2625	0.046*
C32	0.0051(4)	0.0160(3)	−0.2445(3)	0.0460(8)
H32	0.0518	−0.0094	−0.3033	0.055*
C33	0.0155(4)	0.1267(3)	−0.1824(3)	0.0473(8)
H33	0.0683	0.1728	−0.2014	0.057*
C34	−0.0499(4)	0.1695(2)	−0.0941(2)	0.0395(8)
H34	−0.0424	0.2434	−0.0528	0.047*

(b) intermolecular hydrogen bonding between carboxylate O atoms of coordinated HBrip and carboxylate O atoms of free HBrip with $d(\text{O} \cdots \text{O}) = 2.58$ and 2.59 Å; (c) intermolecular hydrogen bonding between carboxy O atoms of free HBrip and N atoms of Hbpp with $d(\text{O} \cdots \text{N}) = 2.71$ Å. A three-dimensional network of hydrogen bonds contributes to the stability of the structure.

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