Jun-Chao Zhang, Jiang-Li Chen and Feng-Mei Nie*

Crystal structure of (pyridine-2-carboxamide- κ^2N,O)-[tris((1*H*-benzo[*d*]imidazol-2-yl)methyl)amine- κ^4N,N',N'',N''']nickel(II) diperchlorate – methanol (1/3), $C_{33}H_{39}Cl_2N_9NiO_{12}$

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.13 × 0.13 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.72 mm ^{−1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	26.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	24869, 7508, 0.061
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5606
$N(param)_{refined}$:	530
Programs:	CrysAlis ^{PRO} [1], SHELX [2], Olex2 [3]

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Ni1	0.36792(4)	0.20909(2)	0.34483(2)	0.01496(12)
Cl1	0.19645(9)	0.48286(4)	0.08139(4)	0.0224(2)
Cl2	0.65082(10)	0.47245(4)	0.34834(5)	0.0325(2)
O1	0.3773(2)	0.30770(10)	0.33064(11)	0.0201(5)
O2	0.1539(3)	0.43044(13)	0.03714(14)	0.0437(7)
O3	0.3171(3)	0.46345(11)	0.12279(14)	0.0364(7)
O4	0.0891(3)	0.49937(13)	0.12676(15)	0.0443(7)
O5	0.2295(3)	0.53884(12)	0.04107(14)	0.0405(7)
O6	0.6867(3)	0.43379(14)	0.28915(15)	0.0562(9)
O7	0.5088(3)	0.49175(13)	0.33814(16)	0.0475(8)
O8	0.7334(3)	0.52928(12)	0.35225(16)	0.0481(8)
O9	0.6718(4)	0.43478(15)	0.41047(15)	0.0685(11)
O10	0.6624(3)	0.42116(13)	0.13939(13)	0.0357(6)
H10	0.6524	0.4249	0.1816	0.054*
O11	0.8109(3)	0.01081(14)	0.19222(14)	0.0420(7)
H11	0.7904	0.0164	0.1505	0.063*
O12	0.7908(4)	0.02604(17)	0.04788(17)	0.0703(10)
H12A ^a	0.7990	0.0445	0.0103	0.105*
H12B ^b	0.7441	0.0462	0.0184	0.105*
N1	0.3663(3)	0.10279(12)	0.36549(14)	0.0167(6)
N2	0.4393(3)	0.21122(12)	0.44610(13)	0.0172(6)
N3	0.5154(3)	0.15908(14)	0.54183(14)	0.0227(6)
H3	0.5372	0.1275	0.5695	0.027*
N4	0.1741(3)	0.19829(12)	0.37920(13)	0.0169(6)
N5	0.0109(3)	0.13245(13)	0.41359(14)	0.0221(6)
H5	−0.0335	0.0971	0.4203	0.027*
N6	0.5563(3)	0.18115(12)	0.31292(13)	0.0182(6)
N7	0.6917(3)	0.10395(12)	0.27458(14)	0.0197(6)
H7	0.7198	0.0660	0.2633	0.024*
N8	0.2944(3)	0.22004(12)	0.23719(13)	0.0167(6)
N9	0.3512(3)	0.39079(13)	0.25572(15)	0.0325(8)
H9A	0.3808	0.4180	0.2871	0.039*

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Abstract

$C_{33}H_{39}Cl_2N_9NiO_{12}$, monoclinic, $P2_1/c$ (no. 14), $a = 9.7478(4)$ Å, $b = 20.6247(7)$ Å, $c = 19.0897(11)$ Å, $\beta = 92.767(5)^\circ$, $V = 3833.4(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0527$, $wR_{ref}(F^2) = 0.1143$, $T = 108.4(2)$ K.

CCDC no.: 1977167

The title complex is shown in the figure (Solvent molecules and counter anions are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tris(2-benzimidazolylmethyl)amine (*ntb*) was synthesized according to the literature [4]. A methanol (10 mL) solution of ligand *ntb* (0.163 g, 0.4 mmol) was dropped slowly into

*Corresponding author: Feng-Mei Nie, Department of Chemistry, Capital Normal University, Beijing 100048, P.R. China, e-mail: niefm@mail.cnu.edu.cn. <https://orcid.org/0000-0001-9150-0729>

Jun-Chao Zhang and Jiang-Li Chen: Department of Chemistry, Capital Normal University, Beijing 100048, P.R. China

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H9B	0.3269	0.4041	0.2143	0.039*
C1	0.4306(4)	0.09211(15)	0.43763(17)	0.0226(8)
H1A	0.3689	0.0664	0.4648	0.027*
H1B	0.5152	0.0678	0.4340	0.027*
C2	0.4609(3)	0.15421(16)	0.47502(16)	0.0194(7)
C3	0.4800(3)	0.25710(16)	0.49635(16)	0.0178(7)
C4	0.5291(3)	0.22458(16)	0.55682(17)	0.0210(7)
C5	0.5766(4)	0.25755(18)	0.61672(18)	0.0279(8)
H5A	0.6098	0.2359	0.6568	0.034*
C6	0.5716(4)	0.32423(19)	0.61314(18)	0.0306(9)
H6	0.6023	0.3481	0.6522	0.037*
C7	0.5221(4)	0.35770(17)	0.55322(17)	0.0251(8)
H7A	0.5195	0.4028	0.5536	0.030*
C8	0.4770(3)	0.32443(16)	0.49347(17)	0.0210(7)
H8	0.4460	0.3462	0.4531	0.025*
C9	0.2198(3)	0.08224(15)	0.36023(18)	0.0213(7)
H9C	0.2066	0.0446	0.3896	0.026*
H9D	0.1935	0.0707	0.3122	0.026*
C10	0.1328(3)	0.13752(15)	0.38376(17)	0.0177(7)
C11	0.0738(3)	0.23537(15)	0.40956(16)	0.0179(7)
C12	−0.0301(3)	0.19433(16)	0.43153(17)	0.0195(7)
C13	−0.1434(4)	0.21731(18)	0.46525(18)	0.0272(8)
H13	−0.2125	0.1896	0.4789	0.033*
C14	−0.1484(4)	0.28336(18)	0.47752(19)	0.0309(9)
H14	−0.2224	0.3006	0.5002	0.037*
C15	−0.0440(4)	0.32484(17)	0.45632(19)	0.0282(8)
H15	−0.0503	0.3690	0.4655	0.034*
C16	0.0679(3)	0.30179(16)	0.42212(17)	0.0229(8)
H16	0.1365	0.3296	0.4081	0.028*
C17	0.4529(3)	0.07253(15)	0.31213(17)	0.0209(7)
H17A	0.3992	0.0654	0.2687	0.025*
H17B	0.4885	0.0312	0.3289	0.025*
C18	0.5683(3)	0.11855(15)	0.30046(16)	0.0183(7)
C19	0.6785(3)	0.20962(15)	0.29481(15)	0.0167(7)
C20	0.7644(3)	0.16157(15)	0.26958(17)	0.0194(7)
C21	0.8916(3)	0.17592(17)	0.24373(18)	0.0256(8)
H21	0.9476	0.1440	0.2260	0.031*
C22	0.9300(4)	0.23998(17)	0.24585(18)	0.0280(8)
H22	1.0140	0.2517	0.2285	0.034*
C23	0.8468(4)	0.28827(17)	0.27326(17)	0.0235(8)
H23	0.8779	0.3309	0.2745	0.028*
C24	0.7206(3)	0.27429(16)	0.29837(16)	0.0207(7)
H24	0.6658	0.3063	0.3169	0.025*
C25	0.2493(3)	0.17512(16)	0.19071(17)	0.0211(7)
H25	0.2512	0.1319	0.2045	0.025*
C26	0.2005(4)	0.18975(17)	0.12360(17)	0.0242(8)
H26	0.1718	0.1568	0.0930	0.029*
C27	0.1945(4)	0.25334(17)	0.10224(18)	0.0263(8)
H27	0.1596	0.2644	0.0576	0.032*
C28	0.2422(3)	0.30070(16)	0.14917(17)	0.0212(7)
H28	0.2416	0.3441	0.1360	0.025*
C29	0.2904(3)	0.28260(15)	0.21572(16)	0.0163(7)
C30	0.3431(3)	0.32880(15)	0.27112(17)	0.0195(7)
C31	0.8014(4)	0.40153(18)	0.1279(2)	0.0344(9)
H31A	0.8245	0.4133	0.0813	0.052*
H31B	0.8094	0.3554	0.1336	0.052*
H31C	0.8630	0.4228	0.1613	0.052*
C32	0.9428(5)	−0.0183(3)	0.1997(2)	0.0664(15)
H32A	0.9640	−0.0276	0.2482	0.100*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H32B	1.0103	0.0109	0.1827	0.100*
H32C	0.9432	−0.0578	0.1731	0.100*
C33 ^a	0.7235(11)	−0.0382(4)	0.0354(4)	0.058(3)
H33A ^a	0.7258	−0.0624	0.0784	0.087*
H33B ^a	0.7715	−0.0617	0.0008	0.087*
H33C ^a	0.6298	−0.0318	0.0190	0.087*
C33 ^b	0.8902(16)	−0.0129(6)	0.0135(6)	0.086(6)
H33D ^b	0.9786	−0.0078	0.0373	0.130*
H33E ^b	0.8950	0.0009	−0.0343	0.130*
H33F ^b	0.8632	−0.0576	0.0147	0.130*

^aOccupancy: 0.563(10), ^bOccupancy: 0.437(10).

the methanol (10 mL) solution of nickel perchlorate hexahydrate (0.147 g, 0.4 mmol) under stirring. After stirring for 30 minutes, pyridine-2-carboxamide (0.049 g, 0.4 mmol) was added to the above solution. The green solution turned to dark-blue immediately. The resulting mixture was stirred for 2 hours at room temperature. Purple crystals were obtained by slowly evaporating the filtrate within five days.

Experimental details

Methyl groups were idealized and refined using rigid groups allowed to rotate about the N—C bond. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 U_{eq} (C) and the U_{iso} values of all other hydrogen atoms were set to 1.2 U_{eq} (C). One methanol molecule was disordered over two sites (C33, C33') (Table 2).

Comment

Pyridine-2-carboxamide (*pia*) is a widely studied pyridine derivative of biological interest. It is also a very interesting ligand which coordinates through the pyridine nitrogen and amide oxygen atoms [5, 6]. Some nickel(II) complexes containing picolinamide have been reported [6–8]. Most of them are bis(*pia*) nickel(II) complexes. It is worthwhile to investigate the coordination behavior of picolinamide with nickel(II) in a rigid tripodal coordination environment. Tris(2-benzimidazolylmethyl)amine (*ntb*) is such a tripodal tetradentate ligand with three benzimidazole side arms [9–11]. Herein, a new nickel(II) complex $[Ni(ntb)(pia)](ClO_4)_2 \cdot 3CH_3OH$ is reported.

Our single crystal diffraction study reveals that the asymmetric unit of the title structure contains a $[Ni(ntb)(pia)]^{2+}$ cation, two perchlorate anions, and three methanol molecules. In the cation $[Ni(ntb)(pia)]^{2+}$, the Ni(II) ion is coordinated by four nitrogens of *ntb* and one *pia* in a bidentate chelating way, forming a distorted octahedral geometry (as shown in the figure, 50% displacement ellipsoids). The equatorial plane is defined by three nitrogen atoms (N2, N4, N6) of

ntb and the pyridine nitrogen N8 atom of *pia* with bond angles in the range of $88.64(10)^\circ$ to $92.72(10)^\circ$. The bond lengths of the three Ni–N (benzimidazole) bonds are $2.023(3)$ Å for Ni1–N2, $2.042(3)$ Å for Ni1–N4, $2.045(3)$ Å for Ni1–N6, respectively. The Ni1–N8 (pyridine) distance is $2.155(3)$ Å which is slightly longer than those observed for the benzimidazole N atoms. The axial sites are occupied by the tertiary amine nitrogen N1 atom of *ntb* and O1 atom of *pia* with the O1–Ni1–N1 bond angle $176.70(9)^\circ$. The bond length of Ni1–O1 is $2.054(2)$ Å and the bond distance of Ni1–N1 is $2.228(3)$ Å, which is longer than those observed for the benzimidazole N atoms. In this complex, *pia* binds to the nickel(II) ion in its usual *pia*-N,O chelation mode. *pia* is nearly coplanar with the benzimidazole group [N2, N3] of *ntb* (dihedral angle 6.19°).

The most striking feature in this complex is that the tripodal *ntb* ligand coordinates to the nickel(II) ion with the three benzimidazole groups in a T shape. Two of the benzimidazole groups of *ntb* are nearly coplanar, while the third is perpendicular to this plane. The dihedral angle between the aromatic moieties containing the rings [N4, N5] and [N6, N7] is 8.53° , while angles of these planes with the third moiety [N2, N3] are 88.46° and 88.55° . This spatial arrangement for *ntb* reflects the great versatility of *ntb* in order to take in the preferred geometry of the nickel(II) ion. This can be observed almost in all nickel(II) complexes of *ntb* [8–13] and also for some other mononuclear metal(II) complexes [14]. As a result of these features, the deviations from an ideal octahedral geometry around the nickel(II) ion are the following: *trans* angles range from $157.36(10)^\circ$ to $176.70(9)^\circ$ and *cis* angles from $77.61(9)^\circ$ to $105.49(10)^\circ$. The distortion within the coordination spheres are mainly caused by the strain imposed by the tripodal *ntb* and by the maintain of the chelate ring of *pia* with the small bite angle of $77.61(9)^\circ$. For the title structure, each mononuclear $[Ni(ntb)(pia)]^{2+}$ cation is interacted with four of its neighbors through π - π stacking of aromatic groups to form a 2D network. Two types of π - π stacking can be observed. The first one involves the benzimidazolic phenyl rings (Cg1 = C11–C12–C13–C14–C15–C16, Cg2 = C19–C20–C21–C22–C23–C24) with centroid to centroid distance of 3.636 Å. The second one involves the benzimidazolic phenyl ring (Cg3 = C3–C4–C5–C6–C7–C8) and the pyridine ring (Cg4 = N8–C25–C26–C27–C28–C29) of *pia* with centroid to centroid distance of 3.629 Å. In addition, extensive hydrogen bonding interactions are observed involving the perchlorate anions and methanol molecules to further stabilize the structure.

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