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The crystal structure of tetrakis(μ_2-(1*H*-benzimidazole-2-methoxo-κ^2*N*,*O*:*O*:*O*)-(*n*-butanol-κ*O*)-chlorido)-tetranickel(II), $C_{48}H_{68}Cl_4N_8O_8Ni_4$

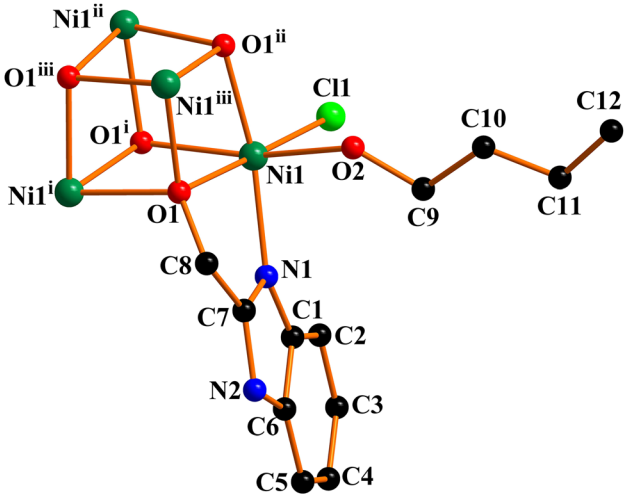

Figure: The cubane cluster structure of I is formed by four Ni(II) ions, four Cl^- anions, four bm and four *n*-butyl alcohol ligands. The H-atoms and the symmetry-related Cl^-, bm and *n*-butyl alcohol ligands are omitted for clarity (symmetry code: i. 1 – *x*, 1.5 – *y*, *z*; ii. 1.25 – *y*, 0.25 + *x*, 1.25 – *z*; iii. *y* – 0.25, 1.25 – *x*, 1.25 – *z*).

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Abstract

$C_{48}H_{68}Cl_4N_8O_8Ni_4$, tetragonal, $I4_1/a$ (no. 88), a = 16.9137(5) Å, c = 19.5028(13) Å, V = 5579.2(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0391, $wR_{ref}(F^2)$ = 0.1221, T = 293 K.

CCDC no.: 1055581

Table 1: Data collection and handling.

Crystal:	Green prism
Size:	0.47 × 0.36 × 0.34 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.58 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	28.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25,550, 3459, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 2685
$N(param)_{refined}$:	165
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4], PLATON [5]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

All chemicals were purchased from commercial sources and used as received. A mixture of $NiCl_2{\cdot}6H_2O$ (0.238 g, 1 mmol) and bm (benzimidazole, 0.150 g, 1 mmol) in 10 mL *n*-butyl alcohol, with a pH adjusted to 8.0 by addition of triethylamine, was poured into a Teflon-lined autoclave (15 mL) and then heated at 433 K for 4 days. After cooling to room temperature at a rate of 283 K h^{-1}, green block-shaped crystals of I were collected by filtration, washed with *n*-butyl alcohol and dried in air. Phase pure crystals were obtained by manual separation (Yield: 65.2 mg ca. 21 % based on bm). Anal. Calc. for I: $C_{48}H_{68}Cl_4N_8O_8Ni_4$ (%) (Mr = 1261.74): C, 45.65; H, 5.39; N, 8.88. Found: C, 45.67; H, 5.38; N, 8.86 %. (CCDC number 1055581).

2 Experimental details

Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with the ShelXL [4] refinement package. Carbon or nitrogen-bound hydrogen atoms were placed in calculated positions (d = 0.93 Å for CH,

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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	0.60101 (16)	0.71142 (16)	0.40250 (14)	0.0431 (5)
C2	0.65484 (19)	0.7668 (2)	0.37804 (17)	0.0562 (7)
H2	0.682989	0.799679	0.407420	0.067*
C3	0.6643 (2)	0.7702 (2)	0.30771 (18)	0.0703 (9)
H3	0.699505	0.806876	0.289538	0.084*
C4	0.6231 (3)	0.7211 (2)	0.26307 (18)	0.0734 (10)
H4	0.631501	0.725966	0.216132	0.088*
C5	0.5703 (2)	0.6655 (2)	0.28654 (16)	0.0623 (8)
H5	0.543079	0.632257	0.256813	0.075*
C6	0.55991 (17)	0.66177 (17)	0.35736 (14)	0.0464 (6)
C7	0.52118 (16)	0.64037 (15)	0.46353 (13)	0.0398 (5)
C8	0.47547 (17)	0.61282 (16)	0.52500 (14)	0.0427 (5)
H8A	0.420399	0.604760	0.513005	0.051*
H8B	0.496834	0.563225	0.541745	0.051*
C9	0.7047 (3)	0.5769 (3)	0.5477 (3)	0.1080 (18)
H9A	0.743068	0.611430	0.526024	0.130*
H9B	0.674549	0.551177	0.511811	0.130*
C10	0.7481 (4)	0.5146 (4)	0.5893 (4)	0.146 (3)
H10A	0.772107	0.541356	0.628054	0.176*
H10B	0.708369	0.479132	0.607866	0.176*
C11	0.8058 (4)	0.4681 (4)	0.5600 (4)	0.171 (3)
H11A	0.846005	0.502223	0.540411	0.205*
H11B	0.782437	0.438104	0.522731	0.205*
C12	0.8439 (3)	0.4129 (3)	0.6075 (4)	0.134 (2)
H12A	0.872889	0.373926	0.582014	0.201*
H12B	0.804331	0.387169	0.634874	0.201*
H12C	0.879504	0.441340	0.636880	0.201*
Cl1	0.71336 (4)	0.79947 (5)	0.55939 (4)	0.04952 (19)
N1	0.57479 (13)	0.69609 (13)	0.46886 (11)	0.0420 (4)
N2	0.51047 (15)	0.61672 (14)	0.39796 (12)	0.0467 (5)
H2A	0.478737	0.580340	0.384100	0.056*
Ni1	0.59216 (2)	0.72735 (2)	0.56929 (2)	0.03550 (13)
O1	0.48216 (10)	0.67187 (10)	0.57579 (9)	0.0365 (4)
O2	0.65445 (14)	0.62170 (13)	0.58722 (12)	0.0582 (5)
H2B	0.626808	0.592473	0.610691	0.087*

d = 0.97 Å for CH_2, *d* = 0.96 Å for CH_3, and *d* = 0.86 Å for NH) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C or N) for –CH, for –NH and for –CH_2, and with U_{iso}(H) set to 1.5U_{eq}(C) for –CH_3. The H atoms of hydroxyl group of *n*-butyl alcohol in I were refined as rotating groups, with d_{O-H} = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O). The structures were examined using the ADDSYM subroutine of PLATON [5] to ensure that no additional symmetry could be applied to the models.

3 Comment

Design and investigation of polynuclear transition metal complexes have received considerable attention because of their different potential applications, such as gas storage [6], separation [7], catalysis [8] and magnet [9]. With the aim of understanding the correlation between structures and kinds of properties, a series of polynuclear complexes have been synthesized, in which the search for key ligands is an important process to advance this investigation [10]. The benzimidazole-based derivatives have received so much interest due to their applications both in coordination chemistry [11] and in medicinal chemistry, such as antibacterial, antiviral and antitumor properties [12]. (1*H*-benzimidazol)-methanol (bm), as an excellent organic ligand with N, O-donor atoms, it can coordinate to the metal-ion to form different structures [13]. As a monodentate ligand it coordinates to the metal ion via the pyridine-type nitrogen to form mononuclear complex [14]. As an bidentate ligand, it coordinates to the metal ion via the pyridine-type nitrogen and the alkoxide oxygen to form mononuclear complex [15], polynuclear complex in which the alkoxide oxygen can bridge more than one metal ion [16]. The other pyrrol-type nitrogen (N–H) is usually involved in hydrogen bond formation with available hydrogen acceptor and/or hydrogen donor sites. Through hydrogen bond and other interactions, the solid state can dictate interesting structure [17]. With the aim of understanding the coordination chemistry, we have recently focussed our research on coordination polymers based on bm ligand. Herein, we describe the synthesis and crystal structure of a cubane Ni(II) cluster, $\{Ni_4(bm)_4Cl_4(C_4H_9OH)_4\}$, prepared by the reaction of $NiCl_2{\cdot}6H_2O$ with bm in *n*-butyl alcohol.

Single-crystal X-ray diffraction analysis reveals that the title structure (I) belongs to the tetragonal space group $I4_1/a$, and contains a cubane cluster with four nickel(II) ion and oxygen atoms from four bm ligands occupying the alternate vertices of the cube. The cubane is formed by four Ni(II) ions, four Cl^- anions, four bm ligands and four *n*-butyl alcohol (Figure 1). The Ni^{II} ion is in a distorted octahedral geometry coordinated by one terminal *n*-butyl alcohol molecule (Ni1–O2, 2.106(2) Å), one Cl^- anion (Ni1–Cl1, 2.3914(8) Å). One benzimidazole N atom (Ni1–N1, 2.049(2) Å) and three μ_3-alkoxide oxygen atoms (Ni1–O1, 2.0908(18) Å; Ni1–O1^i, 2.1205(18) Å; Ni1–O1^{ii}, 2.0617(17) Å, symmetry codes: i. 1 – *x*, 1.5 – *y*, *z*; ii. 1.25 – *y*, 0.25 + *x*, 1.25 – *z*). It must be pointed out that bm exists as a mono-anion and displayed a μ_3–η_3:η_1 coordination mode. It is interesting to note that such a coordinated mode was already observed in $[Ni(bm)Cl(C_2H_5OH)]_4$ [17] and $[Co_4(bm)_4Cl_4(C_3H_7OH)_4]$ [18]. The Ni···Ni distances of I are in the range 3.142–3.210 Å and the magnetic exchange Ni–O–Ni angles of I are in the range 97.41(7)–98.36(7)° [19], showing values for the Ni···Ni ferromagnetic exchange pathways to be dominant, being between 90° and 104° [20]. Complex I further forms a

supramolecular 2–D network through N–H···Cl–M hydrogen bonds (N2–H2a···Cl^{iv}, 3.277(2) Å, 150.4°, symmetry code: (iv) $-y + 5/4$, $x - 1/4$, $z - 1/4$) in the bc plane. It must be mentioned that the importance of such types of N–H···Cl–M hydrogen bonds has already been reported in the literature [21].

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References

1. Oxford Diffraction Ltd. *CrysAlis^{PRO}*; Rigaku Oxford Diffraction, Version 1.171.39.6a: England, 2018.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. SHELXTL – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
6. He Y., Zhou W., Qian G., Chen B. Methane storage in metal-organic frameworks. *Chem. Soc. Rev.* 2014, *43*, 5657–5678.
7. Min K. S., Suh M. P. Self-assembly and selective guest binding of three-dimensional open-framework solids from a macrocyclic complex as a trifunctional metal building block. *Chem. Eur. J.* 2001, *7*, 303–313.
8. Liu J. W., Chen L. F., Cui H., Zhang J. Y., Zhang L., Su C. Y. ChemInform abstract: applications of metal-organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* 2014, *45*, 6011–6061.
9. Hu S., He K. H., Zeng M. H., Zou H. H., Jiang Y. M. Crystalline-state guest-exchange and gas-adsorption phenomenon for a “soft” supramolecular porous framework stacking by a rigid linear coordination polymer. *Inorg. Chem.* 2008, *47*, 5218–5224.
10. Uemura K., Saito K., Kitagama S., Kita H. Hydrogen-bonded porous coordination polymers: structural transformation, sorption properties, and particle size from kinetic studies. *J. Am. Chem. Soc.* 2006, *128*, 16122–16130.
11. Song X. Y., Xu Y. H., Li L. C., Liao D. Z., Jiang Z. H. An unexpected cubane-like nickel(II) tetranuclear complex bridged by the anion of 2-hydroxymethylbenzimidazole: crystal structure and magnetic properties. *Inorg. Chim. Acta* 2007, *360*, 2039–2044.
12. Sigel H. Metal ion complexes of antivirally active nucleotide analogues. Conclusions regarding their biological action. *Chem. Soc. Rev.* 2014, *3*, 191–200.
13. Machura B., Wolff M., Palion J., Kruszynski R. Synthesis, spectroscopic characterization, X-ray structure and DFT calculations of novel mononuclear Re(V) complex with imidazole-derived ligand. *Inorg. Chem. Commun.* 2011, *14*, 1358–1361.
14. Checiriska L., Malecka M., Ochocki J., Kalinowska U. *trans*–Bis(1*H*-benzimidazol-2-yl-methyl-κN_3 diethyl phosphate)-di-chloro-palladium(II) monohydrate. *Acta Crystallogr.* 2004, *E60*, m1558–m1561.
15. Zeng L. L., Leng J. D., Herchel R., Lan Y. H., Powell A. K., Tong M. L. Anion-dependent facile route to magnetic dinuclear and dodecanuclear cobalt clusters. *Eur. J. Inorg. Chem.* 2010, *2010*, 2229–2234.
16. Zhou Y. L., Zeng M. H., Liu X. C., Liang H., Kurmoo M. Exploring the effect of metal ions and counteranions on the structure and magnetic properties of five dodecanuclear CoII and NiII clusters. *Chem. Eur. J.* 2011, *17*, 14084–14093.
17. Zhang S. H., Ma L. F., Zou H. H., Wang Y. G., Liang H., Zeng M. H. Anion induced diversification from heptanuclear to tetranuclear clusters: syntheses, structures and magnetic properties. *Dalton Trans.* 2011, *40*, 11402–11409.
18. Yang L., Zhang S. H., Wang W., Guo J. J., Huang Q. P., Zhao R. X., Zhang C. L., Muller G. Ligand induced diversification from tetranuclear to mononuclear compounds: syntheses, structures and magnetic properties. *Polyhedron* 2014, *74*, 49–56.
19. García-Álvarez A. C., Gamboa-Ramírez S., Martínez-Otero D., Orio M., Castillo I. Self-assembled nickel cubanes as oxygen evolution catalysts. *Chem. Commun.* 2021, *57*, 8608–8611.
20. Tong M. L., Monfort M., Juan J. M. C., Chen X. M., Bu X. H., Ohba M., Kitagawa S. A novel high-spin heterometallic $Ni_{12}K_4$ cluster incorporating large Ni-azide circles and an *in situ* cyanomethylated di-2-pyridyl ketone. *Chem. Commun.* 2005, *2*, 233–235.
21. Wernsdorfer W., Aliaga-Alcalde N., Hendrickson D. N., Christou G. Quantum tunneling in a three dimensional network of exchange coupled single-molecule magnets. *Nature* 2002, *416*, 406–409.