



A Novel Mutually Perpendicular Bicyclo-Shape Tetranuclear Complex Constructed from 2,3-Dihydroxy butanedioic Acid with Pisces Mode

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A new complex $[\text{Ni}_4(\text{dhbd})_4 \cdot 8\text{H}_2\text{O}] \cdot 13\text{H}_2\text{O}$ (**1**) (H_4dhbd = 2,3-dihydroxy butanedioic acid) has been synthesized and its structure ($\text{C}_{16}\text{H}_{16}\text{O}_{45}\text{Ni}_4$, $M_r = 1163.13$) was determined by single-crystal X-ray diffraction analysis. The crystal belongs to the monoclinic system, space group $P_{21/c}$ with $a = 13.700(5)$, $b = 17.143(5)$, $c = 18.599(5)$ Å, $\beta = 96.786(5)$, $V = 4338(2)$ Å³, $Z = 4$, $D_c = 1.781$ g/cm³, $\mu(\text{MoK}\alpha) = 1.839$ mm⁻¹, $F(000) = 2336$, $S = 1.025$, the final $R = 0.0524$ and $wR = 0.1390$ for 9257 reflections with $I > 2\sigma(I)$. The centrosymmetric nickel complex contains a tetranuclear in which four distorted octahedral Ni(II) centers are bridged by the carboxylic oxygen atoms and the hydroxy oxygen atoms of the four 2,3-dihydroxy butanedioic acid with the Pisces mode, featuring a novel mutually perpendicular bicyclo structure. The complex units are further linked to form three-dimensional supramolecular structure *via* the hydrogen bonds between the coordinate water molecules and the plentiful free water molecules. The elemental analysis and optical properties for the complex have been studied.

Keywords: Synthesis, Crystal structure, 2,3-Dihydroxybutanedioic Acid, Bicyclo structure, Nickel(II) complex.

INTRODUCTION

During recent years, the topological mimicking of natural minerals and constructions of novel complexes with new topologies have been extensively investigated not only for the fundamental interest to reveal the intriguing structural diversity and assembling processes of these materials but also for the pragmatic perspective to obtain new functional materials¹⁻⁴. Recent reports indicate that di-/poly-carboxylate ligands have been proved to be a powerful tool in constructing well-ordered multidimensional supramolecular architectures. Owing to their potential applications as zeolite-like solids in catalysis, the use of hydrogen-bond in the ligands as mentioned above to construct supramolecular frameworks with large porosity and channel has become an appealing field⁵⁻⁷. Among these carboxylate-containing ligands, the 2,3-dihydroxy butanedioic acid ligand possesses two terminal carboxyl groups and two hydroxyl groups that may be completely or partially deprotonated, inducing rich coordination quomodos and allowing captivating structures with higher dimensions⁸. Meanwhile, 2,3-dihydroxybutanedioic acid can act as not only hydrogen bond acceptors but also as hydrogen bond donors, depending on the different number of deprotonated hydroxyl and carboxyl groups, to form diverse new extended structures by means of

additional hydrogen-bond interactions⁹. Herein we report the synthesis and characterization of a novel mutually perpendicular bicyclo-shape tetranuclear supramolecular framework $[\text{Ni}_4(\text{dhbd})_4 \cdot 8\text{H}_2\text{O}] \cdot 13\text{H}_2\text{O}$, constructed from 2,3-dihydroxy butanedioic acid (H_4dhbd) ligand with unusual Pisces mode.

EXPERIMENTAL

All chemical reagents were of analytical grade and used without further purification. C, H and N analyses were made on Elementar Vario EL-III elemental analyzer. FT-IR spectra were recorded in the range 4000-400 cm⁻¹ on a Nicolet Avatar-360 spectrometer using a KBr pellet. The single-crystal structure of the compound **1** was determined on a Bruker APXII CCD diffractometer.

The complex $[\text{Ni}_4(\text{dhbd})_4 \cdot 8\text{H}_2\text{O}] \cdot 13\text{H}_2\text{O}$ (**1**) was prepared by the mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.145 g, 0.5 mmol), 2,3-dihydroxy butanedioic acid (0.0750 g, 0.5 mmol) and H_2O (16 mL) was heated at 170 °C for 3 days in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, colourless block crystals were obtained. Yield: 76 %. For $\text{C}_{16}\text{H}_{16}\text{O}_{45}\text{Ni}_4$ Anal. calc. %: C 16.50; H 1.38. Found (%): C 17.65; H 1.51.

X-ray structure determination: A blue colour block single crystal of complex **1** with 0.42 mm × 0.31 mm × 0.21 mm was carefully selected under a polarizing microscope and were mounted on a glass fiber and used for X-ray diffraction analyses. Single crystal structure determination by X-ray diffraction measurements were performed using a Bruker APXII CCD diffractometer with graphite monochromated MoK α ($k = 0.71069 \text{ \AA}$) radiation in the range of $1.50 \leq \theta \leq 28.31^\circ$ ($-17 \leq h \leq 18$, $-22 \leq k \leq 19$, $-23 \leq l \leq 20$) at 293 K. Absorption corrections were applied using the multi-scan technique¹⁰. A total of 24913 reflections including 9839 unique ones were collected, of which 9257 with $I > 2\sigma(I)$ were considered as observed and used in the succeeding refinements. The structure was solved by the Direct Method and refined by full-matrix least-square techniques on F^2 using SHELXL-97¹¹. All of the non-hydrogen atoms were refined anisotropically¹². The H atoms attached to C atoms were positioned geometrically, with Uiso values derived from Ueq values of the corresponding C atom. The final $R = 0.0524$ and $wR = 0.1390$, $S = 1.025$, $(\Delta\rho)_{\max} = 1.649$ and $(\Delta\rho)_{\min} = -1.230 \text{ e/\AA}^3$.

Crystallographic data for the structural analysis(es) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No.: 908416 for the complex **1**.

RESULTS AND DISCUSSION

The single crystal X-ray analysis showed that complex **1** crystallized in monoclinic, space group $P_{21/c}$. The asymmetrical unit of complex **1** contains four Ni²⁺ ion, four dhbd ligand, eight coordinate water and thirteen free water molecules. As shown in Fig. 1, the Ni ion shows a distorted octahedral coordination geometry with four oxygen atoms from the carboxylate and the adjacent hydroxy groups in two different dhbd ligands ($\text{Ni}(1)\text{-O}(13) = 2.020(3) \text{ \AA}$; $\text{Ni}(1)\text{-O}(11) = 2.020(3) \text{ \AA}$; $\text{Ni}(1)\text{-O}(12) = 2.068(3) \text{ \AA}$; $\text{Ni}(1)\text{-O}(9) = 2.080(3) \text{ \AA}$) and two oxygen atoms of the two coordinate water ($\text{Ni}(1)\text{-O}(15) = 2.103(4) \text{ \AA}$; $\text{Ni}(1)\text{-O}(14) = 2.059(4) \text{ \AA}$). The Ni-O (2.007(3)-2.108(3) \AA) bond distances are all in the normal range. Each dhbd anion acts as a μ_2 -bridge with the carboxylate and the adjacent

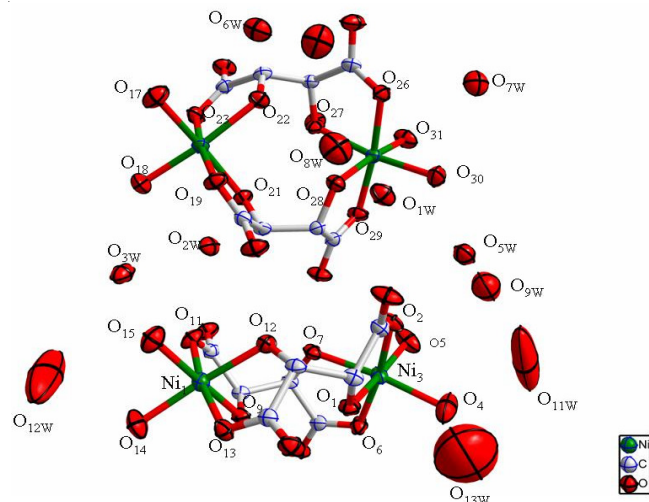


Fig. 1. Coordination geometry of Ni(II) atom in complex **1**. Thermal ellipsoids are drawn at 50 % probability and hydrogen atoms were omitted for clarity. Colour codes: Colour codes: Ni, green; C, gray; O, red

hydroxy groups in the chelate coordination mode, in which the carboxylate groups exhibit a $\mu^1\text{-}\eta^1:\eta^0$ coordination mode¹³. Bidentate-chelating through the dhbd anion, the Ni(II) ions are connected to form the two 12-membered ring, which featuring a novel mutually perpendicular bicyclo-shape (Fig. 2) and the Ni...Ni separation through H₂dhbd chelate anions are 5.0123(13) \AA and 5.0680(13) \AA , respectively.

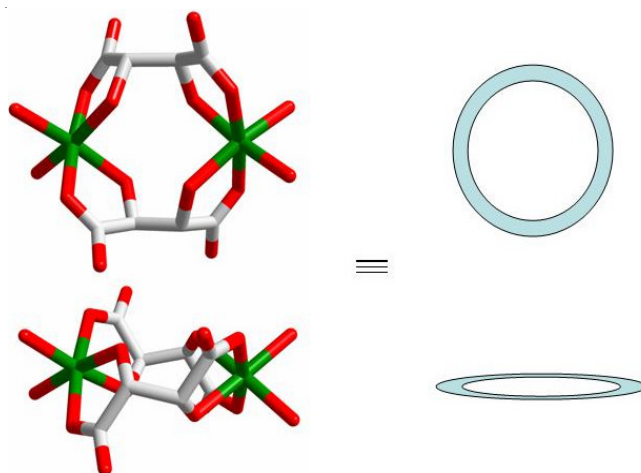


Fig. 2. Scheme of the mutually perpendicular bicyclo-shape. Colour codes: Colour codes: Ni, green; C, gray; O, red

As a result, the mutually perpendicular bicyclo is further linked to a 3D supramolecular structure by the intermolecular hydrogen bonds between the free water molecules and the uncoordinated carboxylate from the dhbd anion ($\text{O}_{(4W)}\text{-H}_{(4)}\dots\text{O}_{(20)} = 2.792(5) \text{ \AA}$, $\text{O}_{(6W)}\text{-H}_{(7)}\dots\text{O}_{(32)} = 2.765(5) \text{ \AA}$, $\text{iii} = 1-x, 1/2 + y, 1/2 - z$). Moreover, as the multiple intermolecular hydrogen bond acceptors and donors ($\text{O}_{(1W)}\text{-H}_{(1)}\dots\text{O}_{(8W)} = 2.720(6) \text{ \AA}$; $\text{O}_{(8W)}\text{-H}_{(8)}\dots\text{O}_{(4W)} = 2.813(6) \text{ \AA}$), the excessive water molecules interacting with the complex from the bicyclo above and below, is shown in Fig. 4, play an important role in the formation of the 3D supramolecular architecture and stabilize the crystal structure. In addition, there are still abundant hydrogen bonds formed by not only water molecules but also hydroxyl group of dhbd ligands in **1** (Table-2). The most striking feature of complex **1** is that, as show in Fig. 4, the 12-membered ring is constructed by the two dhbd ligands with the end to end mode, similar as the Pisces pattern (Fig. 3).

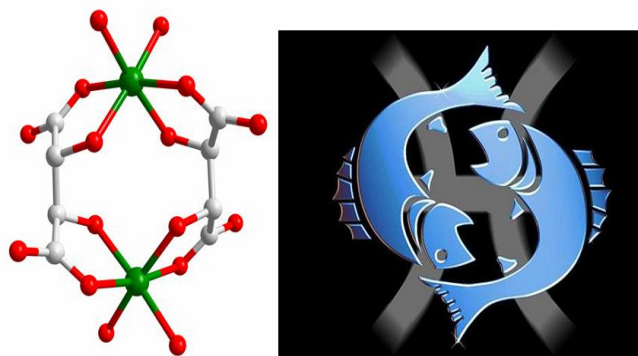


Fig. 3. Illustration of the 12-membered ring with the end to end mode, similar as the Pisces pattern. Colour codes: Colour codes: Ni, green; C, gray; O, red

TABLE-1
 SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg) FOR 1

Bond	Distance (Å)	Bond	Distance (Å)
Ni(1)-O(13)	2.020(3)	Ni(2)-O(27)	2.108(3)
Ni(1)-O(11)	2.020(3)	Ni(3)-O(6)	2.023(3)
Ni(1)-O(12)	2.068(3)	Ni(3)-O(2)	2.029(3)
Ni(1)-O(9)	2.080(3)	Ni(3)-O(5)	2.061(4)
Ni(1)-O(15)	2.103(4)	Ni(3)-O(7)	2.066(4)
Ni(2)-O(26)	2.007(3)	Ni(3)-O(1)	2.071(3)
Ni(2)-O(29)	2.016(3)	Ni(3)-O(4)	2.077(4)
Ni(2)-O(30)	2.046(4)	Ni(4)-O(23)	2.021(4)
Ni(2)-O(31)	2.071(4)	Ni(4)-O(19)	2.029(3)
Ni(2)-O(28)	2.099(3)	Ni(4)-O(18)	2.047(4)
Ni(4)-O(17)	2.068(4)	Ni(4)-O(22)	2.097(3)
Ni(4)-O(21)	2.087(3)	Ni(1)-O(14)	2.059(4)
Angles	ω , deg	Angles	ω , deg
O(13)Ni(1)O(11)	170.62(14)	O(11)Ni(1)O(9)	80.28(13)
O(13)Ni(1)O(14)	92.51(16)	O(14)Ni(1)O(9)	89.59(14)
O(11)Ni(1)O(14)	94.62(17)	O(12)Ni(1)O(9)	92.76(13)
O(13)Ni(1)O(12)	80.31(13)	O(13)Ni(1)O(15)	91.29(15)
O(11)Ni(1)O(12)	92.71(14)	O(11)Ni(1)O(15)	94.85(14)
O(14)Ni(1)O(12)	172.58(15)	O(14)Ni(1)O(15)	89.52(16)
O(13)Ni(1)O(9)	93.71(14)	O(12)Ni(1)O(15)	88.74(15)
O(9)Ni(1)O(15)	174.96(14)	O(26)Ni(2)O(29)	173.33(14)
O(26)Ni(2)O(30)	91.56(16)	O(29)Ni(2)O(30)	93.55(16)
O(26)Ni(2)O(31)	91.64(15)	O(29)Ni(2)O(31)	92.50(14)
O(29)Ni(2)O(31)	92.50(14)	O(26)Ni(2)O(28)	95.87(14)
O(29)Ni(2)O(28)	79.99(13)	O(30)Ni(2)O(28)	88.57(15)
O(31)Ni(2)O(28)	172.48(14)	O(26)Ni(2)O(27)	80.58(13)
O(29)Ni(2)O(27)	94.46(14)	O(30)Ni(2)O(27)	171.81(15)
O(31)Ni(2)O(27)	86.38(15)	O(28)Ni(2)O(27)	94.45(13)
O(6)Ni(3)O(2)	171.90(14)	O(6)Ni(3)O(5)	94.01(15)
O(2)Ni(3)O(5)	91.93(14)	O(6)Ni(3)O(7)	80.90(13)
O(2)Ni(3)O(7)	93.61(14)	O(5)Ni(3)O(7)	90.03(16)
O(6)Ni(3)O(1)	93.75(14)	O(2)Ni(3)O(1)	80.32(13)
O(5)Ni(3)O(1)	172.23(14)	O(7)Ni(3)O(1)	90.99(13)
O(6)Ni(3)O(4)	91.73(17)	O(2)Ni(3)O(4)	93.62(17)
O(5)Ni(3)O(4)	91.4(2)	O(7)Ni(3)O(4)	172.57(16)
O(1)Ni(3)O(4)	88.53(18)	O(23)Ni(4)O(19)	172.29(14)
O(23)Ni(4)O(18)	90.99(17)	O(19)Ni(4)O(18)	93.99(17)
O(23)Ni(4)O(17)	96.34(16)	O(19)Ni(4)O(17)	89.48(15)
O(18)Ni(4)O(17)	90.98(17)	O(23)Ni(4)O(21)	94.35(14)
O(19)Ni(4)O(21)	79.89(13)	O(18)Ni(4)O(21)	88.72(15)
O(17)Ni(4)O(21)	169.31(15)	O(23)Ni(4)O(22)	80.27(13)
O(19)Ni(4)O(22)	94.94(14)	O(18)Ni(4)O(22)	170.97(17)
O(17)Ni(4)O(22)	87.78(15)	O(21)Ni(4)O(22)	94.14(13)

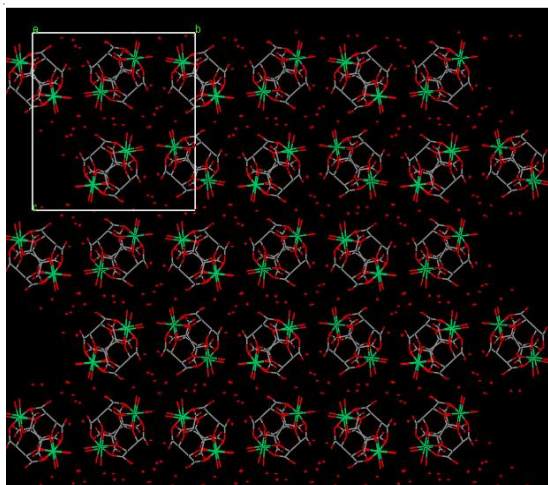


Fig. 4. Molecular packing structure of 1 viewed along the a axis. Colour codes: Ni, green; C, gray; O, red

To our best of knowledge, the mutually perpendicular bicyclo-shape tetranuclear complex featuring Pisces mode is still relatively rare. Selected bond distances and bond angles are shown in Table-1. The hydrogen binding of complex 1 is detailed in Table-2.

The IR spectral data show features attributable to the carboxylate and the hydroxy stretching vibrations of the complex 1. The two absorption bands in the regions 3534-3200 and centered at 1640 and 596 cm^{-1} corresponding to the O-H stretch of the free water and coordinate water ligands, respectively¹⁴. The strong peaks occurring at 1631 and 1526 cm^{-1} indicates the antisymmetric and symmetric stretching vibrations of carboxylate. The separation (Δ) between $\text{msym}(\text{COO})$ and $\text{msym}(\text{COO})$ is 212 cm^{-1} which are more than 200 cm^{-1} , suggesting the carboxylate groups coordinate to metal atoms in mono-dentate mode¹⁵. These results are in agreement with the single-crystal X-ray analysis.

TABLE-2
DISTANCE (nm) AND ANGLES OF HYDROGEN-BONDING FOR COMPLEX 1

D-H	d(D-H)	d(H...A)	∠DHA	d(D...A)
O(1W)-H(1)...O(8W)	0.81	1.91	173	2.720(6)
O(2W)-H(2)...O(23) ⁱ	0.81	2.04	155	2.793(5)
O(3W)-H(3)...O(11)	0.79	2.02	165	2.788(6)
O(4W)-H(4)...O(20)	0.81	2.03	155	2.792(5)
O(5W)-H(5)...O(2)	0.76	2.00	168	2.747(6)
O(5W)-H(6)...O(26) ⁱⁱ	0.84	1.94	171	2.779(5)
O(6W)-H(7)...O(32) ⁱⁱⁱ	0.78	2.01	161	2.765(5)
O(8W)-H(8)...O(4W)	0.73	2.08	174	2.813(6)

Symmetry code: ⁱx, 1/2-y, -1/2+z; ⁱⁱx, 1/2-y, 1/2+z; ⁱⁱⁱ1-x, 1/2+y, 1/2-z

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