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**SPECTRAL AND THERMAL PROPERTIES, AND THE CRYSTAL STRUCTURE OF
1,4,5,8-NAPHTHALENETETRACARBOXYLATE
DINUCLLEAR Ni(II) COMPLEX**

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A novel dinuclear Ni^{II} complex, [Ni₂(ntc)(H₂O)₁₀]·7(H₂O) (**1**), with 1,4,5,8-naphthaene-tetracarboxylate (ntc) has been synthesized and characterized by X-ray diffraction analysis, IR, UV-vis spectra and thermogravimetric analysis. Complex **1** crystallizes in triclinic system, space group *P*-1, *a* = 7.721(3), *b* = 9.458(3), *c* = 11.453(4) Å, α = 114.110(6), β = 92.184(6), γ = 107.472(6)°, *V* = 715.7(4) Å³, *Z* = 1, final *R* = 0.048. Each nickel atom is octahedrally coordinated by five aqua ligands and one oxygen atom of the bridging ntc connecting two nickel atoms. The resulting dinuclear Ni^{II} complex forms a 3D H-bonded network.

Key words: crystal structure; hydrogen bonding; tetracarboxylate; Ni(II) complex.

In recent years, transition metal complexes with aromatic polycarboxylates have received considerable attention due to their intriguing structures and unique functions [1—5]. These complexes raise interest for the long-range magnetic interactions [6], application in bioinorganic chemistry [7], and the preparation of conducting [8] and porous materials [9]. 1,4,5,8-Naphthalenetetracarboxylic acid (H₄ntc) is a typical aromatic polycarboxylic acid which has multiple donor sites for potential coordination. Such ligands may form different bridges between metal centers generating various and sometimes surprising molecular architectures. However, so far there are only a few reports on transition-metal complexes of ntc [10—13]. Here we report the synthesis, spectral and thermal properties, and the crystal structure of a novel Ni^{II} complex with this ligand, [Ni₂(ntc)(H₂O)₁₀]·7(H₂O) (**1**).

EXPERIMENTAL

General methods. Commercially available starting materials of analytical grade were used as received. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. The electronic spectra were recorded on a Hitachi UV-3010 spectrophotometer. IR spectra (KBr pellets) were obtained on a FT-IR 170 SX (Nicolet) spectrometer. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 600 °C, under N₂ with a heating rate of 10 °C/min.

Preparation of [Ni₂(ntc)(H₂O)₁₀]·7(H₂O) (1**).** 1,4,5,8-Naphthalenetetracarboxylic dianhydride (268 mg, 1 mmol) was added to the solution of triethylamine (0.55 ml, 4 mmol) in 30 ml water/methanol (volume ratio 1:9), and the mixture was refluxed for 8 h. An aqueous solution of Ni(NO₃)₂·6H₂O (582 mg, 2 mmol) was then added to the mixture, which was further stirred for 3 h and filtrated. The filtrate was allowed to stand at room temperature until green crystals suitable for single crystal X-ray investigation were obtained in approximately ten days. FT-IR (KBr, cm⁻¹): 3384s, 2267w, 1959w, 1569s, 1426s, 1347s, 1317m, 1222m, 1212m, 848s, 818s, 782s, 682m, 598m. Anal. Calcd (%) for C₁₄H₃₈Ni₂O₂₅ (723.86): C 23.23, H 5.29. Found: C 23.58, H 5.12.

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Table 1

Crystal data and structure refinement summary for **1**

Empirical formula	C ₁₄ H ₃₈ Ni ₂ O ₂₅
Temperature, K	293(2)
<i>M</i>	723.82
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions (Å, deg.)	<i>a</i> = 7.721(3), <i>b</i> = 9.458(3), <i>c</i> = 11.453(4) <i>α</i> = 114.110(6), <i>β</i> = 92.184(6), <i>γ</i> = 107.472(6)
Volume, Å ³	715.7(4)
<i>Z</i>	1
<i>D</i> _{calc} , g/cm ³	1.679
Crystal size, mm	0.20×0.15×0.10
Crystal color and shape	Green block
Reflections collected / unique	4156 / 2909
Max. and min. transmission	0.8703 and 0.7848
Data / restraints / parameters	2909 / 0 / 187
GOOF (on <i>F</i> ²)	1.016
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.048, <i>wR</i> ₂ = 0.105
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.077, <i>wR</i> ₂ = 0.117
Residual peak and hole, e/Å ³	0.47 and -0.47
CCDC deposition N	257956

X-ray crystallographic study of 1. The single crystal X-ray diffraction experiment was carried out on a Bruker Smart 1000 CCD diffractometer at 293(2) K. Data were collected using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) with ω scan mode in the range of $2.42 < \theta < 26.42^\circ$. Unit cell dimensions were refined using least-squares technique. Absorption corrections were applied using SADABS program [14]. The structure was solved by direct methods [15] followed by difference Fourier syntheses. The refinement was performed by full-matrix least-squares method on *F*² using SHELXL-97 program package [16]. H atoms of water were located on a difference Fourier map, while other H atoms were included in calculated positions and refined with fixed thermal parameters each riding on a corresponding parent atom. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 257956, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif. Selected crystallographic data and experimental details for the structure studied are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and general methods. The reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride, which was hydrolyzed in basic condition, with Ni(NO₃)₂·6H₂O in CH₃OH—H₂O solvent gave rise to a novel Ni^{II} complex. The complex was isolated as a crystalline, stable in air product. The IR spectra of the complex showed a strong band at 1569 cm⁻¹ that can be assigned to the ν_{as} vibration of COO⁻ and somewhat weak band at 1347 cm⁻¹ from ν_s vibration. The separation of ν_{as} and ν_s ($\Delta = 222 \text{ cm}^{-1}$) indicates that the coordinated COO⁻ anions are in monodentate coordination mode [17].

The UV-vis spectrum of **1** in methanol was recorded at room temperature. The bands at 212 and 236 nm can be ascribed to π — π transitions of ntc. A shoulder band of 309 nm may arise from the ligand-to-metal charge transfer transition. In addition, two very weak absorptions at 662 and 725 nm may be assigned to the *d*—*d* charge-transfer in the octahedrally coordinated Ni^{II} complex [12].

Thermal analysis. The TG curve of complex **1** consists of two major stages (Fig. 1). The first weight loss, 39.65 % (90—250 °C), approximately corresponds to the release of all water molecules

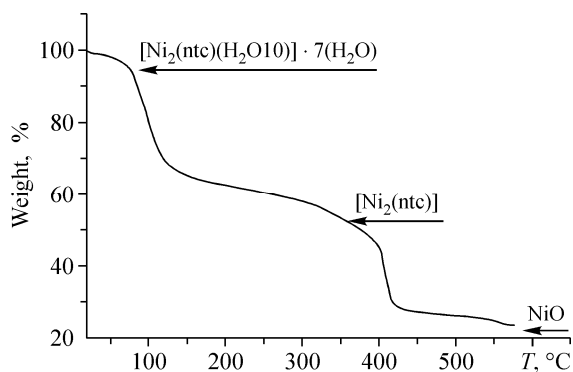


Fig. 1. The TGA curve of **1**

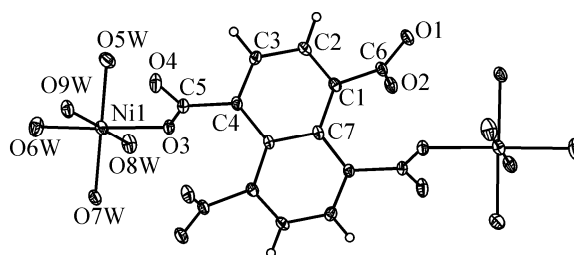


Fig. 2. The thermal ellipsoids plot view with atom labeling (displacement ellipsoids at 30 % probability) of **1** (solvate water molecules are omitted for clarity)

(calculated value 42.27 %). The second weight loss, 36.22 % (250—550 °C), approximately corresponds to the release of 1,4,5,8-naphthalenetetracarboxylic dianhydride (calculated value 37.02 %). The residue does not reveal noticeable weight loss at higher temperatures (up to 600 °C) and is likely to be NiO.

Description of the crystal structure. The thermal ellipsoids plot view of **1** with atom labeling is shown in Fig. 2 and the selected bond lengths and angles are listed in Table 2. The asymmetric unit of **1** consists of one Ni^{II} center, a half of ntc ligand and 3.5 uncoordinated water molecules. The midpoint of the C7—C7ⁱ (*i* = −*x*+2, −*y*+2, *z*) bond is situated at an inversion center. Each Ni^{II} ion is six-coordinated by five aqua molecules and one oxygen atom from ntc to form a slightly distorted octahedron. The *cis* angles around the central Ni^{II} atom vary from 85.25(12) to 95.11(11)°, while the *trans* angles are between 177.61(11) and 179.66(11)°. The average bond length of Ni—OH₂ is 2.054(3) Å and the corresponding Ni—OCO bond length is 2.061(2) Å. The intramolecular Ni1...Ni2 separation is 11.881 Å and the shortest intermolecular Ni...Ni separation is 5.388 Å.

Notably, the ntc ligand is in bis-monodentate coordination mode forming a bridge between two Ni(H₂O)₅ entities. The atom O3 of ntc is coordinated to Ni1 and the bond length of C5—O3 is longer (1.269(4) Å) than the other C—O bonds (average 1.256(4) Å) as expected. The dihedral angles of the COO[−] groups (O3—C5—O4 and O1—C6—O2) with naphthalene ring are 47.6(2)° and 49.8(6)°, respectively. The dihedral angle between the planes of the two carboxylato groups (O3—C5—O4 and O1—C6—O2) is 33.5(3)°. These results show that the carboxylato groups are not in the same plane as the aromatic rings, which is very probably influenced by the formation of the hydrogen-bonding network (Table 3) [18]. The uncoordinated and coordinated water molecules as well as the COO[−] groups lead to complicated 3D hydrogen bonding system as shown in Fig. 3. All the water molecules form strong hydrogen bonds with the carboxylato oxygen atoms or to one another. The O atoms of the four carboxylato group and water molecules act as H-acceptors, while the H atom of the water molecules as H-donors. The O...O distances vary from 2.597(3) to 2.977(6) Å.

Table 2

Selected bond lengths (Å) and angles (deg.) for complex **1**

Ni(1)—O(5W)	2.024(3)	O(5W)—Ni(1)—O(6W)	88.93(12)	O(7W)—Ni(1)—O(9W)	91.90(11)
Ni(1)—O(6W)	2.045(3)	O(5W)—Ni(1)—O(7W)	179.66(11)	O(3)—Ni(1)—O(9W)	95.11(11)
Ni(1)—O(7W)	2.054(3)	O(6W)—Ni(1)—O(7W)	90.86(12)	O(5W)—Ni(1)—O(8W)	91.04(13)
Ni(1)—O(3)	2.061(2)	O(5W)—Ni(1)—O(3)	89.18(11)	O(6W)—Ni(1)—O(8W)	92.43(12)
Ni(1)—O(9W)	2.072(3)	O(6W)—Ni(1)—O(3)	178.07(12)	O(7W)—Ni(1)—O(8W)	88.69(11)
Ni(1)—O(8W)	2.074(3)	O(7W)—Ni(1)—O(3)	91.03(10)	O(3)—Ni(1)—O(8W)	87.19(11)
		O(5W)—Ni(1)—O(9W)	88.36(12)	O(6W)—Ni(1)—O(9W)	85.25(12)

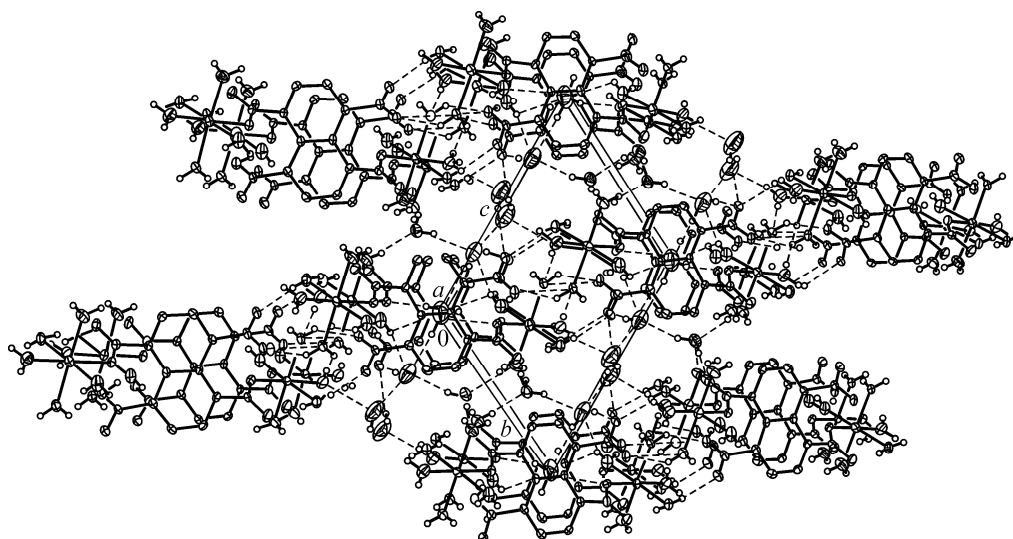


Fig. 3. View of the 3D hydrogen-bonded network in the crystal structure of **1**

Table 3

Hydrogen bonding geometry (Å, deg.) for complex **1**

D—H...A	D—H	H...A	D...A	D—H...A
O(2W)—H(2A)...O(4) ⁱ	0.82	1.91	2.725(5)	177
O(5W)—H(5A)...O(2W) ⁱⁱ	0.82	1.92	2.729(5)	166
O(5W)—H(5B)...O(2W) ⁱⁱⁱ	0.82	1.92	2.739(5)	169
O(7W)—H(7A)...O(2) ^{iv}	0.83	1.92	2.597(3)	138
O(7W)—H(7B)...O(1) ^v	0.84	1.93	2.762(4)	168
O(8W)—H(8B)...O(1W) ^{vi}	0.84	2.20	2.977(6)	155

Symmetry codes: (i) $x-2, y, z+1$; (ii) $x+1, y, z-1$; (iii) $-x-2, y+3, z+1$; (iv) $x, y+1, z+1$; (v) $-x, -y+2, z$; (vi) $x-1, y, z$.

CONCLUSION

A new dinuclear Ni^{II} complex based on the 1,4,5,8-Naphthalenetetracarboxylic acid has been prepared and structurally characterized by single crystal X-ray diffraction analysis. Each Ni^{II} ion in the complex is coordinated by five water molecules and an oxygen atom from ntc to form a slightly distorted octahedron. Some of the coordinated water molecules in the complex might be replaced by other ligands with strong coordinating ability to generate larger coordination architectures. Such studies are under way in our lab.

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