

# Synthesis and Crystal Structures of a mixed-metal Complex with Nitrilotriacetamides

Guichun Sun<sup>a</sup>, Jingwen Ran<sup>b\*</sup>

1. Chemical Engineering College, Huanggang Normal University, Huanggang, 438000, China

2. Hubei Key Laboratory for Processing and Application of Catalytic Materials

<sup>a</sup>email: [shenguichun@qq.com](mailto:shenguichun@qq.com), <sup>b</sup>email: [ranjingwen@hgnu.edu.cn](mailto:ranjingwen@hgnu.edu.cn)

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**Abstract.** A novel complex with nitrilotriacetamides(L) has been synthesized. Single-crystal X-ray diffraction analysis determined the molecular formula as  $C_{12}H_{28}N_8Na_2NiO_{10}$ . The crystal belongs to the triclinic system with P-1 space group. In this molecule, the L ion exhibits an infrequent coordination mode. The nickel center is hexa-coordinated to a slightly distorted octahedral configuration by six nitrogen atoms from two L ligands. The sodium ion is six-coordinated with three oxygen atoms of ligands and three oxygen atoms of water molecules. Two water molecules bridge two  $Na^+$  ions.

## Introduction

Coordination chemistry of imide-based ligands has been extensively studied owing to the fact that they are usually multi-dentate ligands, thus may bridge metal-ions. On the other hand, their metal complexes have been found to be very important so far, as they have a wide range of applications in technology, medicine and agriculture [1-3]. As a result, a series of tripodal imide-derived ligands have been synthesized and employed in fabricating mononuclear or multi-nuclear metal complexes [4-7]. Among numerous tripodal ligands in this category, nitrilotriacetamide and its derivatives are used as classical N-based ligands due to N-atoms coordinating ability. For example, the tris (2-benzylaminoethyl) amine and tris (4-phenyl-3-aza-2-oxobutyl) amine ligands are famous in forming multi-nuclear metal complexes [8, 9] and consequently generate more robust and intricate networks. However, the coordinating ability of O-atoms is ignored. In fact, the introduction of N-donor and O-donor from the nitrilotriacetamide can also coordinate metal ions and generate stable complexes at the same time and result the variation of coordinative mode. Therefore, it is valuable to investigate the coordination chemistry of this ligand. In the paper, we present the synthesis and characterization of the nickel-sodium complex  $[NiNa_2(L)_2(H_2O)_4]_n$  which is assembled into a 3D supra-molecular network via H-bond interactions.

## Experimental

### Materials and physical measurements

All commercially available chemicals were of analysis reagent grade and used without purification. Ligand L was prepared according to the literature method [10]. Elemental analyses were made on a Perkin-Elmer 240C automatic analyzer. UV-Vis spectra were record on a Beijing general analysis TU-1901 spectrometer. IR spectra were recorded on a FT-IR 170 SX (Nicolet) spectro-photometer in the 4000–400  $cm^{-1}$  region with KBr pellets.

### Synthesis of complex

The synthesis of nitrilotriacetamide was carried out according to literature. The title compound was synthesized by adding solid  $Ni(NO_3)_2 \cdot 6H_2O$  (290 mg, 1 mmol) to a solution of ligands (376 mg, 2 mmol) and NaOH (240mg, 6 mmol) in ethanol/water (3:1, 30 ml), then the mixture was stirred for 2 h at room temperature. The solution was filtered and the resulting precipitate was collected and dissolved in a mixture of ethanol and pyridine (3:1 v/v) at 50°C. The solution was allowed to stand in air for 3 d, and blue crystals were formed at the bottom of the vessel on slow evaporation of the solvent

at room temperature. Yield: 48%. Anal. Calcd for  $C_{12}H_{28}N_8Na_2NiO_{10}$ : C 26.25, H 5.14, N 20.41. Found: C 26.64, H 5.29, N 20.55.

### X-ray data collection and crystal structure determination

A single crystal with dimensions of  $0.35\text{mm} \times 0.32\text{mm} \times 0.28\text{mm}$  was selected for X-ray diffraction. The data were collected at 293(2) K on a Bruker APEXII CCD diffraction analysis using graphite-monochromatic  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a  $\omega$  scan mode. A total of 3666 reflections were collected with 2520 unique ones ( $R_{int} = 0.0126$ ). Unit cell dimensions were obtained by full-matrix least-squares refinement. Semi-empirical absorption corrections were applied using the SADABS program [11], the structure was solved by direct methods and refined on F2 by full-matrix least-squares methods using the SHELXL-97 program package [12], and all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of water were located on a difference Fourier map, while other hydrogen atoms were included in the calculated positions and refined with isotropic thermal parameters riding on the corresponding parent atoms. The final refinement converged at  $R = 0.0509$  and  $wR = 0.1478$  ( $w = 1/[\sigma^2(F_o^2) + (0.0929P)^2 + 0.7251P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ). The largest difference peak and hole are 0.901 and  $-0.869 \text{ e/\AA}^3$ , respectively and  $S = 1.07$ .

## Results and discussion

### Structural description

The complex crystallizes in the triclinic system with space group P-1. Molecular structure and labeling scheme for  $[NiNa_2(L)_2(H_2O)_4]_n$  are shown in Fig. 1. In the structural unit of the molecule, there are two ligands anions and four coordinated water molecules. Selected bond lengths and bond angles for the title complex are given in Table 1.

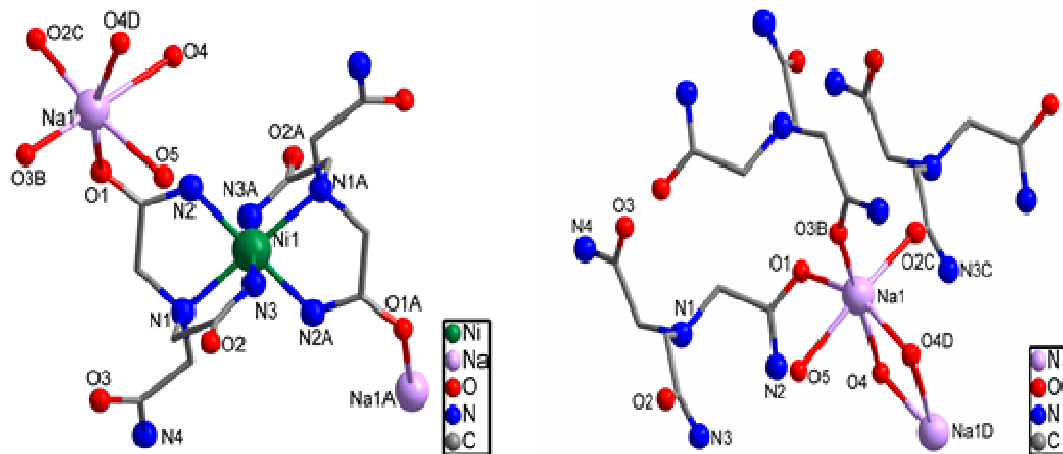


Fig. 1 Coordination environment around the Ni (II) and Na (I) ion in the complex at 30% probability thermal ellipsoids

The centre nickel cation is hexa-coordinated to six N atoms from two nitrilotriacetamides and forms a slightly distorted octahedral configuration which is centrosymmetric as Ni (II) occupies an inversion center. The Ni atom is coordinated in a planar geometry by the N atoms of imides. Two trans axial sites of this coordination environment are occupied by N atoms of tertiaryamines. In the equatorial plane the Ni-N distance is 2.049(2) Å for Ni(1)–N(2) and 2.022(2) Å for Ni(1)–N(3), The axial Ni-N bond is appreciably extended which is 2.136(2) Å for Ni(1)–N(1). The angles formed by the nickel ion and two adjacent coordination N atoms are close to 90, with a deviation of 1.28. Two diagonally coordinated N atoms and the central nickel are co-linear. Each sodium cation is coordinated by three oxygen atoms from three acyl groups and three water molecules, with the Na–O bonds falling in the range of 2.283(3)–2.568(3) Å (average 2.443 Å), longer than Ni(1)–N. So each sodium cation is in octahedron geometry. Two adjacent O (4) from water molecules bridge two sodium cations from different unit. As

the Na–O (4) bonds, the complex forms a 3D unit structure, the complex is best described as [NiNa<sub>2</sub> (L) 2(H<sub>2</sub>O) 4] n, which represents the repeating unit of the 3D structure.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)-N(3)	2.022(2)	Ni(1)-N(2)	2.049(2)	Ni(1)-N(1)	2.136(2)
Na(1)-O(3)#2	2.283(3)	Na(1)-O(2)#3	2.335(3)	Na(1)-O(5)	2.385(3)
Na(1)-O(4)#4	2.390(3)	Na(1)-O(1)	2.568(3)	Na(1)-O(4)	2.689(3)
Angle	(°)	Angle	(°)	Angle	(°)
N(3)#1-Ni(1)-N(3)	180.0	N(3)#1-Ni(1)-N(2)#1	91.28(11)	N(3)-Ni(1)-N(2)#1	88.72(11)
N(3)#1-Ni(1)-N(2)	88.72(11)	N(3)-Ni(1)-N(2)	91.28(11)	N(2)#1-Ni(1)-N(2)	180.00(1)
N(3)#1-Ni(1)-N(1)#1	82.83(9)	N(3)-Ni(1)-N(1)#1	97.17(9)	N(2)#1-Ni(1)-N(1)#1	80.74(9)
N(2)-Ni(1)-N(1)#1	99.26(9)	N(3)#1-Ni(1)-N(1)	97.17(9)	N(3)-Ni(1)-N(1)	82.83(9)
N(2)#1-Ni(1)-N(1)	99.26(9)	N(2)-Ni(1)-N(1)	80.74(9)	N(1)#1-Ni(1)-N(1)	180.00(1)
O(3)#2-Na(1)-O(2)# 3	98.38(1)	O(3)#2-Na(1)-O(5)	94.68(11)	O(2)#3-Na(1)-O(5)	166.34(1)
O(3)#2-Na(1)-O(4)# 4	91.45(11)	O(2)#3-Na(1)-O(4)# 4	99.64(1)	O(5)-Na(1)-O(4)#4	83.99(10)

Symmetry transformation: #1 -x+2, -y+1, -z #2 -x+2, -y+1, -z+1 #3 x, y+1, z #4 -x+3, -y+2, -z #5 x, y-1, z

Each sodium cation is coordinated by three oxygen atoms from three acyl groups and three water molecules, with the Na–O bonds falling in the range of 2.283(3)–2.568(3) Å (average 2.443 Å), longer than Ni(1)-N. So each sodium cation is in octahedron geometry. Two adjacent O (4) from water molecules bridge two sodium cations from different unit. As the Na–O (4) bonds, the complex forms a 3D unit structure, the complex is best described as [NiNa<sub>2</sub> (L) 2(H<sub>2</sub>O) 4] n, which represents the repeating unit of the 3D structure.

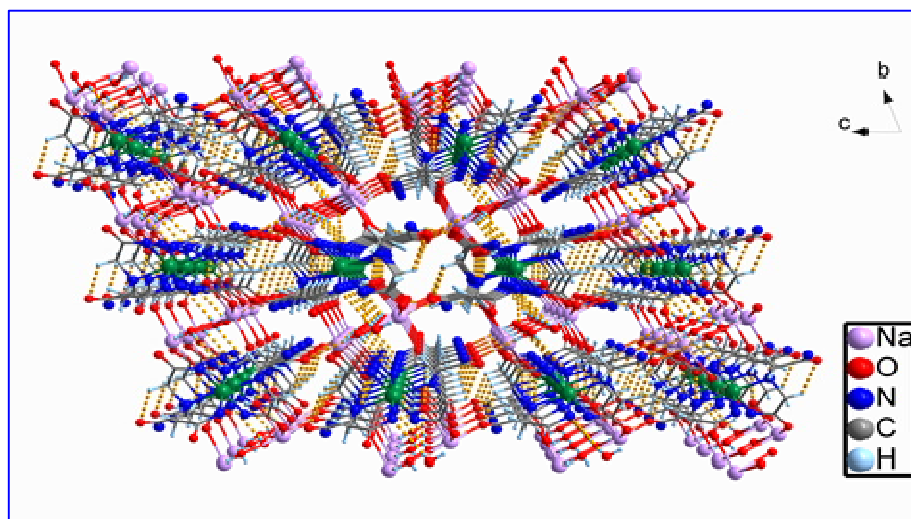


Fig. 2 Packing diagram of  $[\text{NiNa}_2(\text{L})_2(\text{H}_2\text{O})_4]_n$  in the crystal viewed along the a-axis

### Spectrum analysis of the complex

The UV/Vis spectra of complex in methanol shows a wide peak at 292 nm. The peak should be ascribed to the  $n \rightarrow \pi^*$  orbital transition for imide group. IR spectrum of the complex shows strong absorption peaks at 1631.7  $\text{cm}^{-1}$ , which is assigned to the  $\nu \text{C}=\text{O}$  absorption of imide group. A band at 3531  $\text{cm}^{-1}$  could be assigned to the stretching vibration ( $\nu\text{OH}$ ) of coordinated water molecules, and the broad shape of this band suggests the existence of H-bonds. The weak bands of  $\nu\text{N}-\text{H}$  are observed at 3420  $\text{cm}^{-1}$  for and 3321  $\text{cm}^{-1}$ . The bands at 2927.7 and 1452.3  $\text{cm}^{-1}$  are assigned to the stretching vibrations and out-of-plane bending of C–H bond for methylene.

### Conclusion

A novel nickel coordination complex with nitrilotriacetamides was prepared and characterized in this paper. The molecule unit is consisted by a central Ni (II), two  $\text{Na}^+$ , two nitrilotriacetamides ligands and four coordinated water molecules. Central Ni (II) is coordinated to a slightly distorted octahedron by two nitrilotriacetamides.  $\text{Na}^+$  is coordinated by oxygen atoms from imides group and water. The UV-Vis and IR spectrum show the different groups.

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