

Crystal Structure, Theoretical Analyses and Thermodynamic Properties of a Ni(II) Complex Based on ONO Donor Tridentate Acylhydrazone

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Summary: A novel complex $[\text{Ni}(\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3)_2] \cdot \text{H}_2\text{O} \cdot (\text{CH}_3\text{OH})$ (1) ($\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3 = 2$ -[(4-nitrobenzoyl)-hydrazone]-propionic acid) has been prepared by reaction of NiCl_2 with $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ in mixed solvent of methanol and water. The Ni(II) complex in octahedral geometry was characterized by elemental analysis and X-ray single crystal diffraction. Isothermal titration calorimetry (ITC) was performed to observe the reactions between Ni(II) and $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ in methanol solvents. The results showed that the binding constant (K_a), enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) of the system are 5.2×10^5 , $-11.82 \text{ kJ} \cdot \text{mol}^{-1}$, $69.78 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $-32.62 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. In addition, the structure was optimized and frontier molecular orbital (FMO) of (1) were analyzed by B3LYP and HF methods with 6-31g level.

Keywords: Crystal structure, acylhydrazone, Quantum Chemical, Isothermal titration calorimetry.

Introduction

Hydrazones were established in 1884 by Emil Fischer which can be classified as a type of Schiff base compounds [1]. Acylhydrazone is a kind of compound containing $-\text{CO}-\text{NH}-\text{N}=\text{C}-$ group, formed by the reaction of hydrazide with different aldehydes or ketones. Because of the disappearance of free $-\text{NH}_2$ in hydrazide, acylhydrazone has lower toxicity than hydrazide [2]. Acylhydrazone is a potential therapeutic drug. Almost all literatures of acylhydrazone mention its extensive biological and pharmaceutical activities[3-6], such as *anti-fungal*, *anti-convulsant*, *anti-bacterial*, *anti-platelets*, *anti-malarial*, *anti-inflammatory*, *anti-tuberculosis*, *anti-cancer* and insecticidal activities and so on. Moreover, the oxygen of acyl group and nitrogen of imino group can act as coordination atoms and form stable chelating five-membered ring with metal ions. In addition, the coordination modes of acylhydrazone are varied, such as keto-mode [7], enol-mode [8] and dehydroconjugated-mode [9]. It can coordinate to metal ions in neutral form [10], negative monovalent form [11] or negative divalent form [12] with different coordination numbers. Therefore, acylhydrazone and their derivatives have been widely used in coordination chemistry [13-16]. Literature survey reveals that the reports for acylhydrazone complexes mostly focused on crystal structure and biological activity, but there were few reports on the theoretical analyses and thermodynamic properties. However, the theoretical analyses and thermodynamic properties were also very important

properties for this kind of compounds. So in this paper, we report the crystal structure, theoretical analyses and thermodynamic properties of a Ni(II) complex with $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$.

Experimental

Materials and Measurements

Pyruvic acid($\text{CH}_3\text{COCO}(\text{OH})$) was of BC grade, 4-nitrobenzhydrazide and ethanol were of AR grade. All reagents were commercial grade and were used as received. IR were recorded in KBr pellets using Nicolet 380 in the range of $4000-400 \text{ cm}^{-1}$. Elemental analysis of the target compounds were measured on PE-2400 elemental analyzer. The X-ray single crystal diffraction experiment was performed on a Bruker Smart-1000 CCD X-ray single-crystal diffractometer. Isothermal titration calorimetry (ITC) experiments were developed on a nano ITC (TA instruments, New Castle, DE).

Synthesis

The ligand $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ was synthesized according to the literature [17] with minor modifications. Briefly, $\text{CH}_3\text{COCO}(\text{OH})$ (0.2951 g, 3.35 mmol), 4-nitrobenzhydrazide (0.5887 g, 3.2 mmol) and 100 mL ethanol were added to a 250 mL flask and refluxed for about 3 h, and a white precipitate was obtained. Then the precipitate was filtered, washed with ethanol and vacuum dried. Yield: 72.8%. Anal. calcd for $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$: C, 47.81; H, 3.61; N,

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16.73. Found: C, 47.82; H, 3.65; N, 16.74.

Synthesis of the title complex $[\text{Ni}(\text{C}_{10}\text{H}_8\text{O}_5\text{N}_3)_2] \cdot \text{H}_2\text{O} \cdot (\text{CH}_3\text{OH})$ (1). 2.0 mmol $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ and 1.0 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL methanol and 20 mL distilled water, respectively. Then the two solutions were added into a 250 mL flask with continuous stirring and refluxed for about 4 h. The filtrate was evaporated at room temperature, and green prism crystals suitable for X-ray diffraction were obtained after two weeks. Yield: 30 %. Anal. Calc. for $\text{C}_{21}\text{H}_{22}\text{N}_6\text{NiO}_{12}$: C, 41.41; H, 3.64; N, 13.80. Found: C, 41.35; H, 3.52; N, 13.77.

Crystal structure determination

The single crystal suitable for X-ray analysis is glued to a fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-K α radiation, $k = 0.071073$ nm. The intensity data are collected at $T = (298 \pm 2)$ K. The structure is solved by direct methods and expanded using Fourier techniques with SHELXL-97 program. The non-hydrogen atoms are refined anisotropically by full-matrix least-squares calculations on F^2 .

Quantum Chemical Investigation

The geometry structure optimization, the energies of frontier molecular orbital (FMO) containing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were performed by virtue of Gaussian 09 program package via both the HF and B3LYP methods at 6-31g level.

Isothermal titration calorimetry (ITC) experiment

ITC experimental method was developed on a nano ITC (TA instruments, New Castle, DE) according to the literature [18]. Ethanol was injected into reference cell and used as reference solution. All reaction solutions were degassed for 10 minutes before use. NiCl_2 solution (36.81 mM) was used as titrant and was titrated into $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ solution (1.93 mM). Both NiCl_2 and $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ were dissolved in ethanol. Equilibration time was set to 1800 s. Injection interval was set to 600 s. Stirring rate was set to 300 rpm. Titration reaction temperature was set to 25 °C. In order to ensure the accuracy of the

experimental data, the experiment was repeated three times. Raw data were corrected for the heat of dilution, which was measured by performing a titration of NiCl_2 (36.81 mM) into buffer using identical experimental settings. All experimental data were analyzed by Nano-analyzer software.

Results and Discussion

Crystal structure

Fig. 1 is crystal structure of (1). Selected bond lengths and angles of (1) are given in tables 2. Hydrogen-bonding data is given in table 3.

From Fig. 1, it can be found that the coordination number (CN) of Ni(II) in the asymmetric unit of the complex is 6, which consists of two nitrogen atoms (N3 and N6) and four oxygen atoms (O3, O4, O8 and O9), respectively. The carboxyl oxygen atoms (O4 and O9) of $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ coordinate with Ni(II) ions in a monodentate form.

The protons of the two $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ are removed and in the form two negative monovalent anions when they coordinate with Ni(II) ions. Comparing with the distances of carbon oxygen single bond (1.42 Å) and carbon oxygen double bond (1.23 Å), the bond lengths of O(3)-C(7) and O(8)-C(17) are 1.238(3) Å and 1.230(3) Å, respectively, indicating that the two bonds are double linkage and the two ligands both coordinate with Ni(II) in keto-form. The bond angle of $\angle\text{O8-Ni1-O9}$, $\angle\text{O8-Ni1-O3}$, $\angle\text{O3-Ni1-O4}$, and $\angle\text{O4-Ni1-O9}$ are $90.02(7)^\circ$, $91.02(7)^\circ$, $90.46(7)^\circ$, and $90.27(7)^\circ$, respectively. The sum of the four bond angles is 361.77° , which is close to 360° . Therefore, it can be seen that a distorted plane is formed by O8-O3-O9-O4. The bond angle of $\angle\text{N6-Ni1-N3}$ is $175.54(7)^\circ$, which is closed to 180° . Thus, N6 and N3 occupies the axial position. So the coordination geometry of Ni1 ion can be described as a slightly distorted octahedron. Because nickel is a nitrophilic element, so the mean bond length of Ni-N bonds (1.98565 Å) is shorter than that of Ni-O bonds (2.0703 Å). There are six intermolecular hydrogen bonds in the complex. Both the lattice water and methanol molecules act as a hydrogen bond donor/acceptor to form several hydrogen bonds. These hydrogen bonds link the molecules to infinite 2-D framework (Fig. 2).

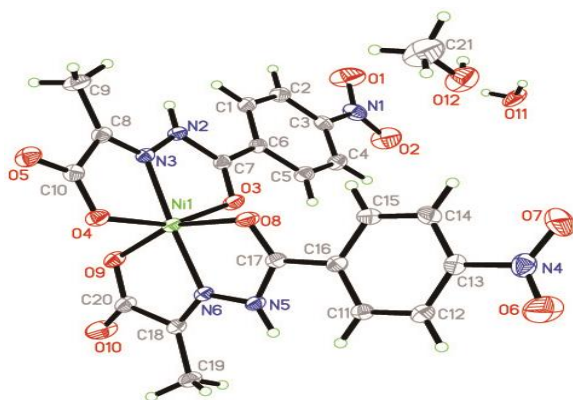


Fig.1: Crystal structure of (1).

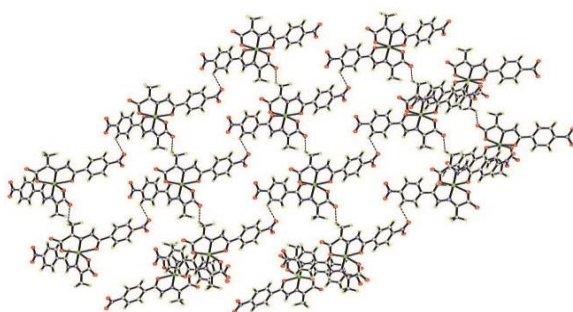


Fig.2: 2-D framework of (1).

Quantum Chemical

To get a deeper insight into the geometries, structural parameters and role of HOMO and LUMO frontier orbitals of (1), DFT calculations at the HF/6-31g level and B3LYP/6-31g level were performed and the optimized geometries and HOMO and LUMO frontier orbitals of (1) were obtained. Some of the bond lengths and angles are listed in Table 2 and table 3. The optimized geometry of (1) is displayed in Fig. 3. From the comparison of experimental data with calculated ones, it can be found that the data of bond lengths obtained from two different methods are in conformity with those observed from experiment, while the error of bond angle is a bit larger. The largest deviations of the bond lengths calculated by B3LYP/6-31g and HF/6-31g are 0.2050 Å and 0.2232 Å, respectively. However, the largest deviations of the bond angles calculated by B3LYP/6-31g and HF/6-31g are 12.08° and 12.77°, respectively. The reason for the deviation may be that the solvent molecules in the cell are ignored for the convenience of calculation. The 3D plot of FMO of (1) was shown in Fig. 4. As shown in

Fig. 4, the negative one is in green and the positive phase is presented in red. The HOMO is located over the carboxyl group and the LUMO is located over the benzene ring, which show that charges transfer occurs in the molecule. According to literature [17], the HOMO and LUMO energies of the free ligand $C_{10}H_9O_5N_3$ are calculated to be -7.622 eV and -3.169 eV, in which the energy gap is 4.453 eV. However, for (1), the HOMO and LUMO energies are -0.23574 eV and -0.13872 eV, respectively. The energy gap value is only 0.09702 eV, which is much smaller than free ligand $C_{10}H_9O_5N_3$, which indicates that electrons in (1) can be excited much easier from the ground state to excited state than in the ligand $C_{10}H_9O_5N_3$.

Table-2: Selected bond lengths (Å) for (1).

Bond	Experimental data (Å)	Calculated data (Å)	
		B3LYP/6-31g	HF/6-31g
Ni(1)-N(6)	1.9807(17)	2.0020	2.1124
Ni(1)-N(3)	1.9902(17)	2.0020	2.1124
Ni(1)-O(4)	2.0395(16)	2.0043	2.0210
Ni(1)-O(9)	2.0601(16)	2.0043	2.0209
Ni(1)-O(3)	2.0734(16)	2.2784	2.2966
Ni(1)-O(8)	2.1078(16)	2.2787	2.2967
O(3)-C(7)	1.238(3)	1.2608	1.2364
O(8)-C(17)	1.230(3)	1.2608	1.2364
Largest deviation		0.2050	0.2232

Table-3: Selected bond angles (°) for (1).

Bond angle	Experimental data (°)	Calculated data(°)	
		B3LYP/6-31g	HF/6-31g
N(6)-Ni(1)-N(3)	175.54(7)	174.18	173.564
N(6)-Ni(1)-O(4)	105.19(7)	96.65	99.704
N(3)-Ni(1)-O(4)	79.24(7)	79.88	76.414
N(6)-Ni(1)-O(9)	79.08(7)	79.88	76.414
N(3)-Ni(1)-O(9)	101.24(6)	96.62	99.754
O(4)-Ni(1)-O(9)	95.27(7)	107.35	108.04
N(6)-Ni(1)-O(3)	98.30(7)	109.60	113.70
N(3)-Ni(1)-O(3)	77.25(7)	74.69	71.16
O(4)-Ni(1)-O(3)	156.32(7)	151.977	145.05
O(9)-Ni(1)-O(3)	92.03(7)	87.33	90.22
N(6)-Ni(1)-O(8)	76.79(6)	74.69	71.17
N(3)-Ni(1)-O(8)	102.86(6)	109.63	113.65
O(4)-Ni(1)-O(8)	90.46(7)	87.34	90.20
O(9)-Ni(1)-O(8)	155.87(6)	151.96	145.05
O(3)-Ni(1)-O(8)	92.01(7)	90.21	91.03
Largest deviation		12.08	12.77

Table-4: Hydrogen Bonds.

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
O(11)-H(11B)...O(12)#1	0.809(10)	1.943(12)	2.745(3)	171(3)
O(11)-H(11A)...O(5)#2	0.812(10)	1.976(12)	2.781(3)	171(4)
O(12)-H(12A)...O(4)#3	0.82	2.61	3.250(3)	135.5
O(12)-H(12A)...O(5)#3	0.82	2.09	2.883(3)	162.5
N(2)-H(4A)...O(9)#4	0.86	2.03	2.749(2)	140.1
N(5)-H(2A)...O(11)#5	0.86	1.95	2.731(3)	151.0

Symmetry transformations used to generate equivalent atoms: #1 x, y, z+1
#2 -x+1, -y, -z+1 #3 x+1, y, z #4 -x, -y, -z+1 #5 -x+1, -y+1, -z+1

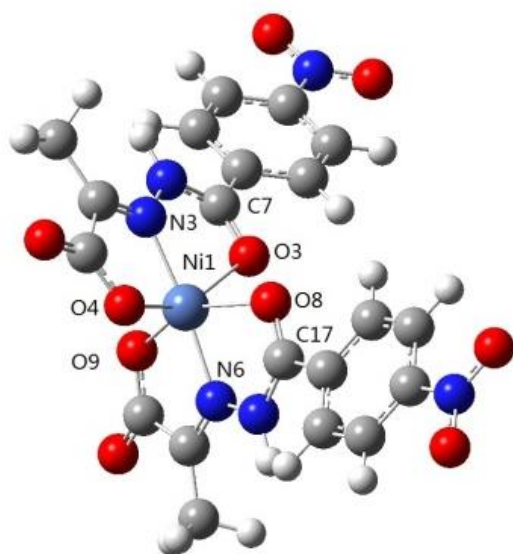


Fig. 3: The optimized geometry of (1).

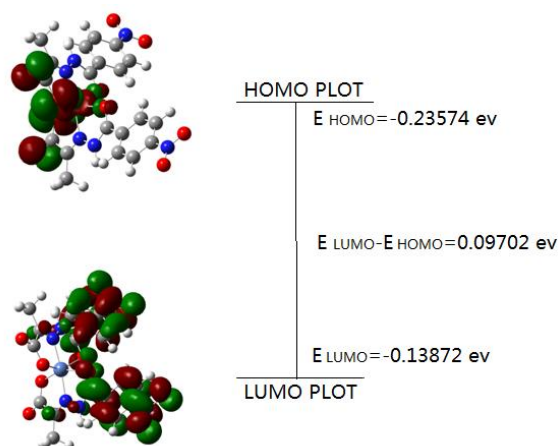
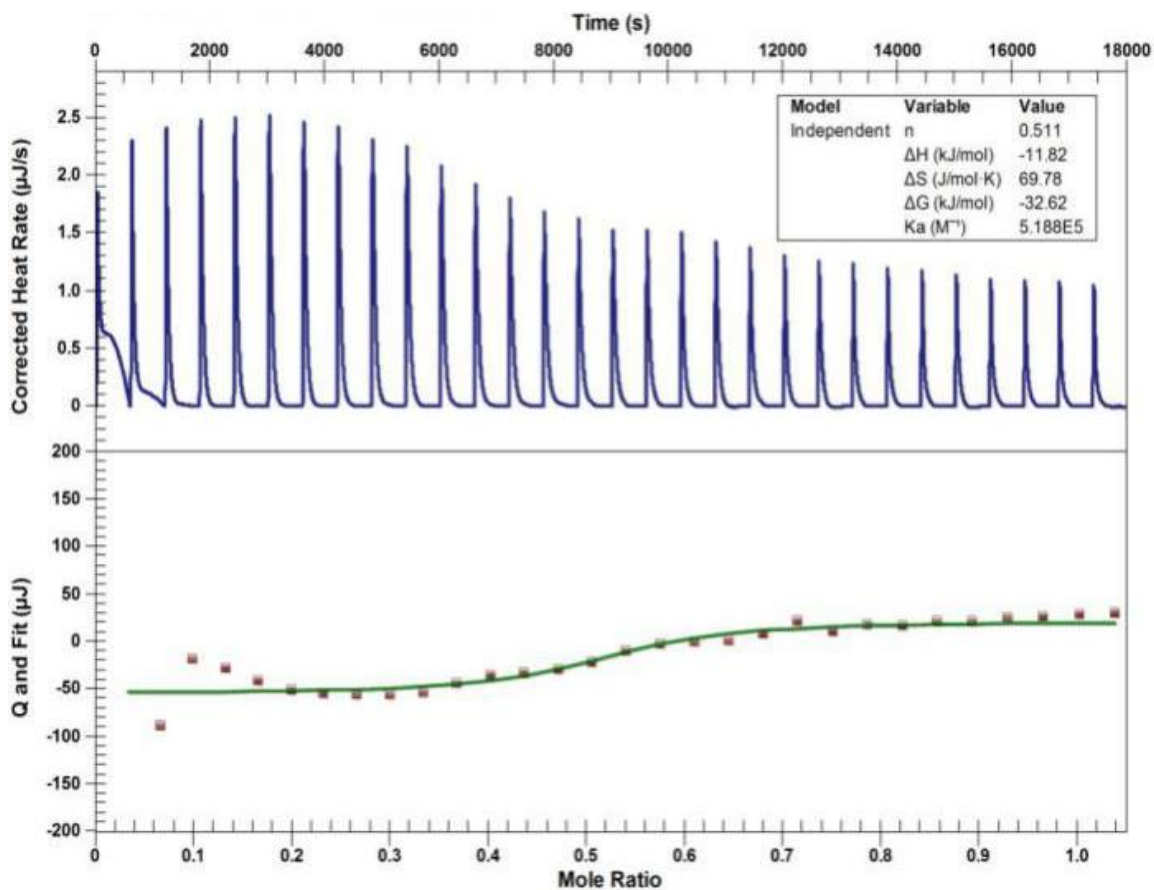


Fig. 4: The 3D plots of the frontier molecular orbital for (1).

Fig. 5: The ITC titration curve of NiCl_2 with the ligand $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$.

Isothermal titration calorimetry (ITC) experiment

For (1), the titration curve shows that the reaction is a heat released and entropy increased process at 298 K, as characterized by an upward tendency of the ITC shown in Fig. 5. The value of ΔG is negative, which implies the process is spontaneous in experiment condition. The binding constant $K_a = 5.2 \times 10^5$, indicating that (1) is very stable. The values of ΔH and ΔS are $-11.82 \text{ kJ}\cdot\text{mol}^{-1}$ and $69.78 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, which suggests that the reaction is a process driven by entropy and entropy. The titration results show that the binding mole ratio of Ni(II) ion to ligand $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ is 0.511, which indicate that (1) is a 1:2 complex. The result of binding mole ratio is agree with X-ray single crystal diffraction experiment

Conclusions

A Ni(II) complex with the general formulas $[\text{Ni}(\text{C}_{10}\text{H}_8\text{O}_5\text{N}_3)_2]\cdot\text{H}_2\text{O}\cdot(\text{CH}_3\text{OH})$ (1) involving a tridentate acylhydrazone ligand were prepared and characterized. The coordination geometry of Ni(II) ion can be described as a slightly distorted octahedron coordination geometry. Molecular structure studies on (1) have been performed using HF/6-31g method and B3LYP/6-31g method. The energy gap is much smaller compared to the free ligand. ITC experiment results have been shown a 1:2 (M:L) coordination, which is agree with crystal structure analysis. Microcalorimetry reveals that the reaction between Ni(II) ion and $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ is a process driven by both entropy and entropy.

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