*Nickel(II) Complex with Dibromotyrosine*

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# Synthesis, Crystal Structure and Theoretical Calculation of a Novel Nickel(II) Complex with Dibromotyrosine and 1,10-Phenanthroline

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A new complex [Ni(phen)($C_9H_8Br_2NO_3$)$_2$·2CH$_3$OH·2H$_2$O] [phen: 1,10-phenanthroline $C_9H_8Br_2NO_3$: 3,5-dibromo-L-tyrosine] was synthesized and characterized by IR, elemental analysis and single crystal X-ray diffraction. X-ray crystallography shows that Ni(II) ion is six-coordinated. The Ni(II) ion coordinates with four nitrogen atoms and two oxygen atoms from three ligands, forming a mononuclear Ni(II) complex. The crystal crystallizes in the Orthorhombic system, space group $P2_12_12$ with $a$ = 12.9546 Å, $b$ = 14.9822 Å, $c$ = 9.9705 Å, $V$ = 1935.2 Å, $Z$ = 1, $F(000)$ = 1008, $S$ = 0.969, $\rho_{calcd}$ = 1.742 g·cm$^{-3}$, $\mu$ = 4.688 mm$^{-1}$, $R_1$ = 0.0529 and $wR_2$ = 0.0738 for 3424 observed reflections ($I > 2\sigma(I)$). Theoretical study of the title complex was carried out by density functional theory (DFT) method and the B3LYP method employing the 6-3l+G* basis set. The energy gap between HOMO and LUMO indicates that this complex is prone to interact with DNA. CCDC: 908041.

**Key Words :** Nickel(II) complex, 3,5-Dibromo-L-tyrosine, 1,10-Phenanthroline, Crystal structure, Quantum chemistry calculation

## Introduction

A large amount of experiments have elucidated that metal complexes have potential applications as antibacterial, anti-cancer and antiviral agents.[1,2] Due to their high bioactivity,[3] heterogeneous catalysis ability[4] and magnetism,[5] many complexes have attracted enough attention of the chemists all over the world. 3,5-Dibromo-L-tyrosine exists in abundance in marine sponges like sponges of the Aplysina species. The ecological function of these brominated secondary metabolites is not clear yet, but they may play a role in chemical defense and deterrence.[6-10] 1,10-Phenanthroline belongs to polydentate ligands, which can chelate with transition metal cations to form metal complexes. Bioactivity experiments indicate that complexes with 1,10-phenathroline as a second ligand have more potent DNA binding capability and anti-cancer activity than the complex without 1,10-phenathroline.[11,12] The particular bioactivity may due to the planar property of 1,10-phenathroline. Further investigation on the interaction of DNA with small molecules are important to the design of new types of pharmaceutical molecules and more efficient antitumor drugs.[13]

Recently, a series of crystal structures of nickel complexes have been reported, which have demonstrated promising cytotoxic activity and a good activity in the inhibition of tumor cell proliferation.[14-16] In this paper, we describe the preparation, characterization and crystal structure of a novel nickel complex, [Ni(phen)($C_9H_8Br_2NO_3$)$_2$·2CH$_3$OH·2H$_2$O], which was derived from 3,5-dibromo-L-tyrosine, 1,10-Phenanthroline and Ni(II). Additionally, based on crystal data, density functional theory (DFT) studies of the title complex were performed using the Gaussian 03 program suite. The

Mulliken charges distribution, molecular total energy and frontier molecular orbital energies of the complex were discussed.

## Experimental

**Materials and Physical Measurement.** All chemicals used in this work were analytical grade and used without further purification. Infrared spectrum was recorded as KBr pellets on the Nicolet 170SX spectrometer in the 4000-400 cm$^{-1}$ region. Elemental analysis (C, H, and N) was performed in a model 2400 PerkinElmer analyzer. The X-ray diffraction data were collected on an Enraf-nonius CAD-4 diffractometer. Optimizations of geometrical structures of the title complex was carried out by DFT B3LYP method. The 6-31+G* basis set was used for C, N, O atoms, while the Effective Core Potential (ECP) and valence double-$\zeta$ LANL2DZ basis set was used for Ni and Br atoms. Atom coordinates used in the calculations were from crystallographic data, and a molecule in the unit cells was selected as the initial model. All calculations were conducted on a Pentium IV computer using Gaussian 03 program.[17]

**Synthesis of the Title Complex.** 3,5-Dibromo-L-tyrosine (0.339 g, 1.0 mmol) and potassium hydroxide (0.056 g, 1.0 mmol) were dissolved in 30 mL of methanol with magnetic stirring, and then 1.0 mmol (0.248 g) of nickel acetate dissolved in 10 mL of anhydrous methanol were added dropwise to the solution. The mixture was stirred at 50 ºC for 4 h. Then, 1,10-phenanthroline (0.198 g, 1.0 mmol) dissolved in 10 mL of anhydrous methanol was added dropwise to the above solution and stirred for 4 h at 50 ºC. The resulting solution was cooled at room temperature and then filtered.

The filtrate was left for slow evaporation at room temperature. The purple block-shaped crystals formed two weeks later. Anal.Calcd. (%) for $C_{32}H_{36}Br_4N_4NiO_{10}$: C, 37.88; H, 3.58; N, 5.52. Found (%): C, 37.77; H, 3.62; N, 5.59. IR (KBr): 3353 br, 1587 s, 1546 m, 1478 m, 1424 m, 1400 m, 1240 m, 1145 m, 1061 m, 815 m, 713 w, 585 m, 486 m.

**Crystallographic Data Collection and Structure Determination.** The single crystal with dimensions of 0.50 × 0.40 × 0.30 mm was mounted on an Enraf-Nonius CAD4 X-ray single-crystal diffractometer. All data were collected at 298(2) K with a graphite monochromatized MoKα radiation (λ = 0.71073 Å) by using *an ω–2θ* scan mode. A total of 9416 reflections were collected in the range of $2.45 \le θ \le 25.01°$ ($-15 \le h \le 13$, $-8 \le k \le 17$, $-10 \le l \le 11$), in which 3424 were independent with $R_{int} = 0.1189$, of which 2011 with $I > 2σ(I)$ were considered to be observed and used in the subsequent refinements. The structure was solved using SHELXS-97.[18] The non-hydrogen atoms were defined with Fourier synthesis method. Positional and thermal parameters were refined by full-matrix least-squares method to convergence. The final cycle of refinement gave $R = 0.0529$, $wR = 0.0738$ [$I > 2(I)$] and $R_1 = 0.1168$, $wR_2 = 0.0859$ (total reflections) ($w = 1/[σ^2(F_o^2) + (0.0002P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 0.969$, $(Δρ)_{max} = 0.657$, $(Δρ)_{min} = -0.597$ e/Å$^3$ and $(Δ/σ)_{max} = 0.000$. A summary of the key crystallographic information is given in Table 1.

**IR Spectroscopy.** The single broad band at 3300 cm$^{-1}$ is attributed to the stretching vibration of dissociative water ν(OH). The absorption maximum at 3353 cm$^{-1}$ is assigned to NH$_2$ in the metal complex, which shifted to lower wave numbers, confirming the involvement of the imine N atom in coordination to metal ion. The bands at 1587 and 1400 cm$^{-1}$ are assigned to antisymmetrical and symmetrical stretching vibrations of acetate anions, ν$_{as}$(COO$^-$) and ν$_s$(COO$^-$). The bands at 585 and 486 cm$^{-1}$ are assigned to ν(Ni–N) and ν(Ni–O), respectively. Bands at 815 and 713 cm$^{-1}$ can be assigned to the bending vibration skeletal of 1,10-phenanthroline. Compared with the free 1,10-phenanthroline (850 and 726 cm$^{-1}$), they both shift to lower wave numbers, indicating that the two N atoms of 1,10-phenanthroline have coordinated to the central nickel ion.

## Results and Discussion

**Structural Descriptions of the Complex.** The selected bond lengths and bond angles are given in Table 2. The hydrogen bond distances of the complex are given in Table 3. The crystal structure is shown in Figure 1. The one-dimensional chain structure, two-dimensional layer structure and the packing diagram of the title complex are shown in Figure 2, Figure 3 and Figure 4, respectively. The crystallographic structural analysis reveals that the title complex is coordinated by six atom, namely, two nitrogen atoms and two carboxylic oxygen atoms from 3,5-dibromo-L-tyrosine, and two nitrogen atoms from 1,10-phenanthroline, forming a neutral 4N+2O complex. The crystal structure of this complex is shown in Figure 1. The corresponding O(1)–Ni(1)–N(2)(169.8°) and O(1A)–Ni(1)–N(2A) (169.8°) bond angles (Table 2) are both less than 180°, and the bond angles N(1)–Ni(1)–N(2)(94.5°), N(1)–Ni(1)–N(2A)(94.9°), O(1)–Ni(1)–N(1)(80.38°), O(1A)–Ni(1)–N(1)(91.47°) bond angles are all different from the ideal value of 90°, indicating that the central Ni(II) adopts a distorted octahedral geometry. Four atoms N(1), N(2A), O(1A) and N(1A) define the basal plane, while N(2) and O(1) are located in the apical positions of the octahedral structure. The bond lengths of Ni(1)–O(1) and Ni(1)–O(1A) are both 2.046 Å, which is in good agreement with the values of Ni–O bond lengths reported in the literature.[19] As for the Ni–N bond lengths, Ni(1)–N(1) (2.096 Å) and Ni(1)–N(1A) (2.096 Å) are shorter than Ni(1)–N(2) (2.104 Å) and Ni(1)–N(2A) (2.104 Å), suggesting that the coordination ability of the 3,5-dibromo-L-tyrosine nitrogens N(1) and N(1A) is stronger than that of the 1,10-phenanthroline N(2) and N(2A).

As shown in Figure 4, the O–H⋯O intermolecular hydrogen bonds are formed between the water, methanol and the complex molecules. These hydrogen-bonded chains propagate along the *c*-axis. The hydrogen bonds are listed in Table 3. A three-dimensional network is assembled through hydrogen bonds. The crystal packing is effectively stabilized by these hydrogen-bonding interactions in the crystal.

**Quantum Chemistry Calculation.** Some optimized parameters are shown in Table 2. It is found that some bond lengths and bond angles data gained from the calculations have subtle difference with those obtained from the determination. On the basis of molecular orbital theory, the HOMO, LUMO and the vicinal molecular orbital affect the property of coordination mostly. We obtained molecular

**Table 1.** Summary of crystallographic data for the complex

| | |
|---|---|
| Empirical formula | $C_{32}H_{36}Br_4N_4NiO_{10}$ |
| Formula weight | 1015.00 |
| Temperature/K | 298 |
| Crystal system | Orthorhombic |
| Space group | P2$_1$2$_1$2 |
| *a*/Å | 12.9546(11) |
| *b*/Å | 14.9822(13) |
| *c*/Å | 9.9705(7) |
| Volume/Å$^3$ | 1935.2 |
| *F*(000) | 1008 |
| Crystal size/mm$^3$ | 0.50 × 0.40 × 0.30 |
| Θrange for data collection/(°) | 2.45 to 25.01 |
| Limiting indices | $-15 \le h \le 1$ |
| | $-8 \le k \le 17$ |
| | $-10 \le l \le 11$ |
| Reflections collected / unique | 9416 / 3424 [R(int) = 0.1189] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Calculated density/Mg/m$^3$ | 1.74 |
| Data / restraints / parameters | 3424 / 0 / 232 |
| Goodness-of-fit on $F^2$ | 0.969 |
| Final R indices [$I > 2σ(I)$] | $R_1 = 0.0529$, $wR_2 = 0.0738$ |
| R indices (all data) | $R_1 = 0.1168$, $wR_2 = 0.0859$ |
| Largest diff. peak and hole/e$^{-3}$ | 0.657 and −0.597 |

**Table 2.** Selected bond lengths ($\overset{\prime}{A}$) and bond angles (°) of the complex obtained from experiment and calculations

| | | | | | |
|---|---|---|---|---|---|
| Ni(1)-O(1) | 2.044(5) | 1.892 | Br(2)-C(8) | 1.908(7) | 1.969 |
| Ni(1)-O(1A) | 2.044(5) | 1.892 | N(1)-C(2) | 1.476(8) | 1.470 |
| Ni(1)-N(1) | 2.096(4) | 2.561 | N(2)-C(14) | 1.326(10) | 1.330 |
| Ni(1)-N(1A) | 2.096(4) | 2.561 | N(2)-C(10) | 1.363(8) | 1.360 |
| Ni(1)-N(2) | 2.104(6) | 1.965 | O(1)-C(1) | 1.259(7) | 1.300 |
| Ni(1)-N(2A) | 2.104(6) | 1.965 | O(2)-C(1) | 1.262(8) | 1.234 |
| Br(1)-C(6) | 1.880(8) | 1.952 | O(3)-C(7) | 1.366(9) | 1.356 |
| | | | | | |
| O(1)-Ni(1)-O(1A) | 96.9(2) | 95.9 | C(2)-N(1)-Ni(1) | 111.9(4) | 99.5 |
| O(1)-Ni(1)-N(1) | 80.4(18) | 76.4 | C(14)-N(2)-C(10) | 118.0(7) | 118.8 |
| O(1A)-Ni(1)-N(1) | 91.5(18) | 80.6 | C(14)-N(2)-Ni(1) | 129.6(5) | 128.7 |
| O(1)-Ni(1)-N(1A) | 91.5(18) | 80.6 | C(10)-N(2)-Ni(1) | 112.4(6) | 112.5 |
| O(1A)-Ni(1)-N(1A) | 80.4(18) | 76.4 | C(1)-O(1)-Ni(1) | 117.6(5) | 126 |
| N(1)-Ni(1)-N(1A) | 167.8(3) | 145.4 | O(1)-C(1)-O(2) | 123.3(7) | 122.5 |
| O(1)-Ni(1)-N(2) | 169.8(2) | 173.4 | O(1)-C(1)-C(2) | 118.5(7) | 118.3 |
| O(1A)-Ni(1)-N(2) | 92.0(2) | 90.5 | O(2)-C(1)-C(2) | 118.2(6) | 119.1 |
| N(1)-Ni(1)-N(2) | 94.5(2) | 99.2 | N(1)-C(2)-C(1) | 110.6(5) | 112.6 |
| N(1A)-Ni(1)-N(2) | 94.9(2) | 99.2 | N(1)-C(2)-C(3) | 114.0(5) | 113.8 |
| O(1)-Ni(1)-N(2A) | 92.0(2) | 90.4 | C(9)-C(8)-Br(2) | 118.5(7) | 119.1 |
| O(1A)-Ni(1)-N(2A) | 169.8(2) | 173.4 | N(2)-C(10)-C(10A) | 117.8(5) | 115.8 |
| N(1)-Ni(1)-N(2A) | 94.9(2) | 99.2 | N(2)-C(10)-C(11) | 121.0(8) | 123.6 |
| N(1A)-Ni(1)-N(2A) | 94.5(2) | 99.2 | N(2)-C(14)-C(13) | 122.7(9) | 121.7 |
| N(2)-Ni(1)-N(2A) | 79.5(4) | 83.3 | | | |

**Table 3**. Hydrogen bond distances ($\overset{\prime}{A}$) and angles (°) of the complex

| D–H⋯A | d(D-H) | d(H⋯A) | d(D⋯A) | < DHA |
|---|---|---|---|---|
| N1–H1A⋯O5[i] | 0.900 | 2.346 | 3.232(8) | 168.290 |
| N1–H1A⋯O3[i] | 0.900 | 2.571 | 3.186(8) | 126.080 |
| O3–H3⋯Br2 | 0.820 | 2.630 | 3.139(6) | 122.000 |
| O3–H3⋯O5 | 0.820 | 1.960 | 2.664(6) | 144.000 |
| O4–H4⋯O1 | 0.820 | 2.370 | 3.108(9) | 151.000 |
| O4–H4⋯O2 | 0.820 | 2.120 | 2.798(9) | 140.000 |
| O5–H5C⋯O2[ii] | 0.850 | 1.954 | 2.803(7) | 177.450 |
| O5–H5D⋯O4[iii] | 0.850 | 2.001 | 2.850(8) | 177.310 |
| C5–H5⋯O2 | 0.930 | 2.600 | 3.230(8) | 126.000 |
| C15–H15⋯O1[iv] | 0.930 | 2.600 | 3.487(8) | 161.000 |

Symmetry code: (*i*) –x+3/2, y–1/2, –z+1; (*ii*) x, y, z–1; (*iii*) x+1/2, –y+3/2, –z+1; (*iv*) –x+1, –y+1, z–1.
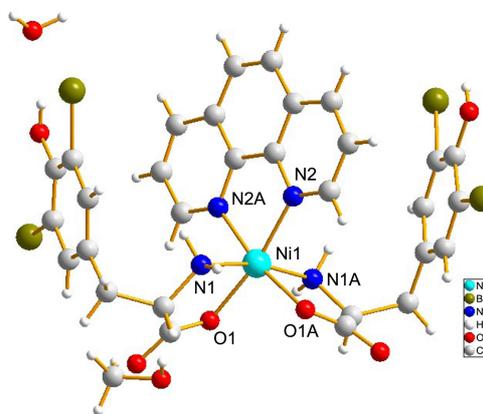


**Figure 1.** The Crystal structure of [Ni(phen)(C₉H₈Br₂NO₃)₂· 2CH₃OH·2H₂O]. All hydrogen atoms and methanol molecules were omitted for clarity.
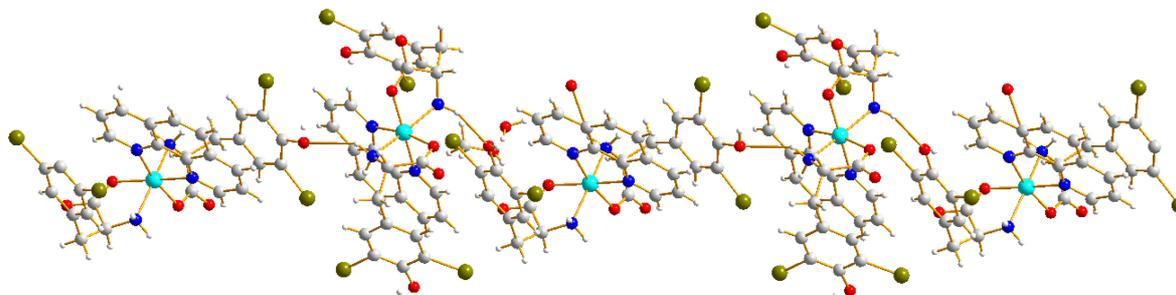


**Figure 2.** 1D chain structure of [Ni(phen)(C₉H₈Br₂NO₃)₂·2CH₃OH·2H₂O] linked by O–H⋯O hydrogen bonds.

total energy and frontier molecular orbital energies of the complex by (DFT) B3LYP method. The total energy of the complex is −55783.406 eV. The energies of HOMO, HOMO-1 and HOMO-2 are −5.279, −6.204, −6.394 eV, respectively,
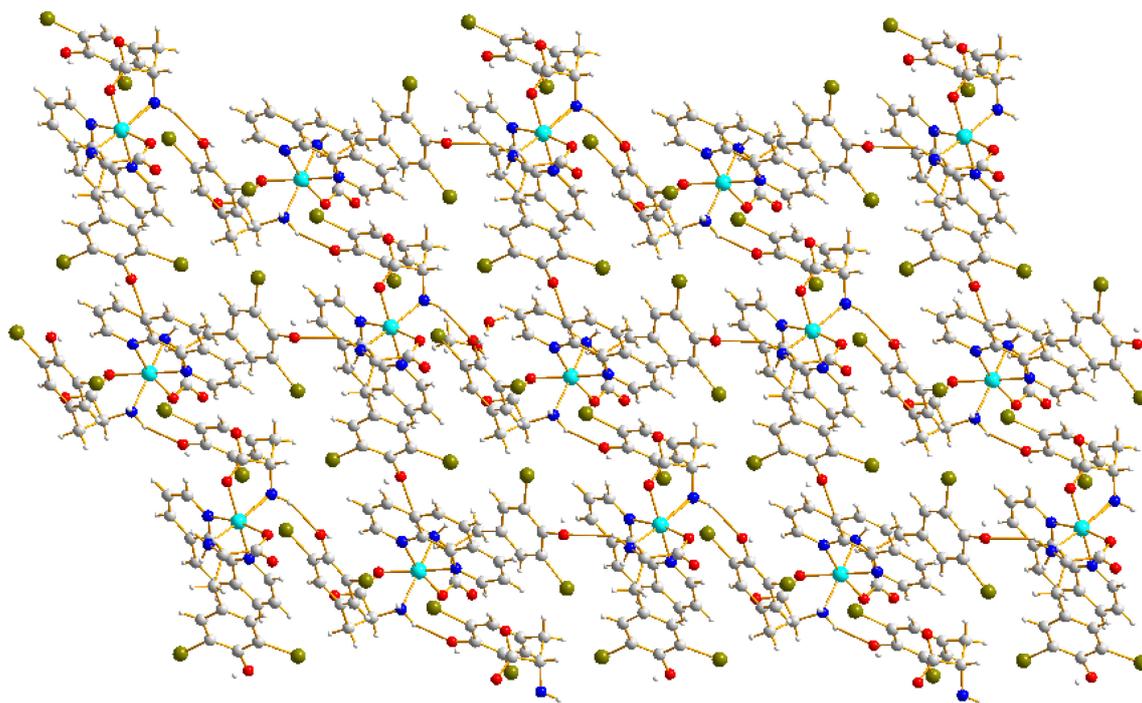
**Figure 3.** 2D layer structure of [Ni(phen)(C$_9$H$_8$Br$_2$NO$_3$)$_2$·2CH$_3$OH·2H$_2$O].
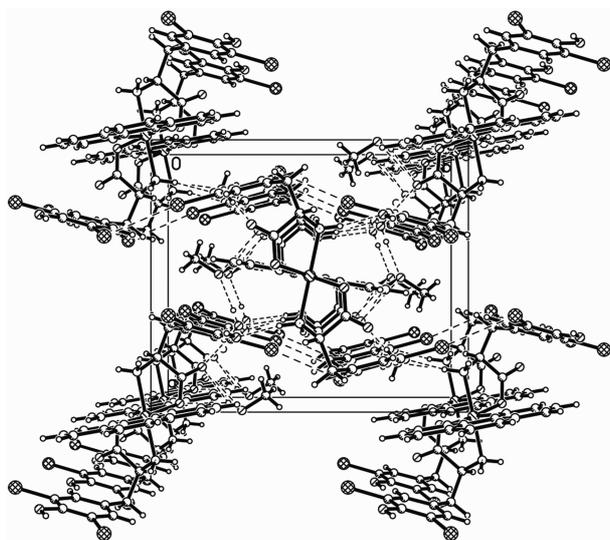


**Figure 4.** The packing diagram of the unit cell.

**Table 4.** Part Mulliken charges of the complex

| Atom | Charge | Atom | Charge |
|------|--------|------|--------|
| Ni | 1.117 | C5 | −0.224 |
| O1 | −0.768 | C5A | −0.224 |
| O1A | −0.768 | C6 | −0.168 |
| O2 | −0.686 | C6A | −0.168 |
| O2A | −0.686 | C7 | 0.281 |
| O3 | −0.689 | C7A | 0.281 |
| O3A | −0.689 | C8 | −0.180 |
| N1 | −0.941 | C8A | −0.180 |
| N1A | −0.941 | C9 | −0.243 |
| N2 | −0.471 | C9A | −0.243 |
| N2A | −0.473 | C10 | 0.187 |
| Br1 | 0.093 | C10A | 0.194 |
| Br1A | 0.093 | C11 | −0.006 |
| Br2 | 0.061 | C11A | −0.007 |
| Br2A | 0.061 | C12 | −0.160 |
| C1 | 0.805 | C12A | −0.160 |
| C1A | 0.805 | C13 | −0.261 |
| C2 | −0.184 | C13A | −0.261 |
| C2A | −0.184 | C14 | 0.073 |
| C3 | −0.482 | C14A | 0.073 |
| C3A | −0.482 | C15 | −0.109 |
| C4 | −0.047 | C15A | −0.109 |
| C4A | −0.047 | | |

the energies of LUMO, LUMO+1 and LUMO+2 are −2.966, −2.830, −1.905 eV, respectively. The energy gap between HOMO and LUMO orbitals is 2.313 eV. The dipole moment is 12.7380 D. The total energy of the title complex and the energies of HOMO, LUMO and their neighboring orbitals are all negative, which indicate that the compound is stable.[20-22] The orbit graphs of the HOMO, LUMO, HOMO-1 and LUMO+1 shown in Figure 5 visually indicate the contributions of the atoms. Geometrical structure of the complex is related to the distribution of Mulliken charge. Table 4 indicates part of the Mulliken charges of the complex.

From Mulliken charge data, we can know that all O and N atoms carry negative charges, the C atoms linking with O and N atoms carry positive charges, and the C atoms linking with H atoms carry negative charges. These negative charged O and N atoms are easy to coordinate with the positive
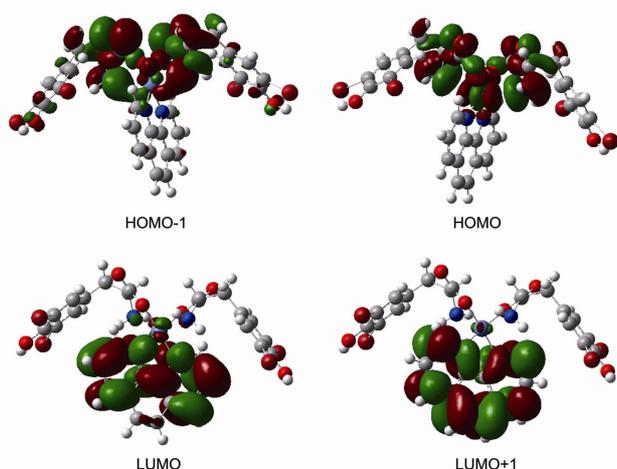
**Figure 5.** The orbit graphs of the HOMO, LUMO, HOMO-1 and LUMO+1.

charged metal ion. The charge of Ni decreases from +2 to +1.117, which indicates that part of the electrons have transferred from N and O atoms to Ni ion and the stable nickel complex was formed.

There are π-π stacking interactions between the complex and DNA-base-pairs while the complex binds to DNA in an intercalation (or part intercalation) mode. Many theoretical studies[23] have shown the following idea: (1) The DNA base-pairs are electron donors and an intercalated complex is an electron acceptor. (2) The energies of HOMO and HOMO-x (x: small integer) of DNA base-pairs are rather high, and their components are predominately distributed on DNA base-pairs. (3) The energies of LUMO and LUMO+x of the intercalated complex are all negative and rather low, and even quite lower than those of HOMO-x of DNA base-pairs, and their components are generally distributed on the main-ligand of the complex. From the above analysis, we can see that the key factor affecting DNA-binding afnities of the complex should be the planarity, energy and population of the lowest unoccupied molecular orbital (LUMO, even and LUMO+x) of the intercalated molecules. Japanese scholar Kurita[24,25] had obtained the energies of molecular frontier orbitals in DNA base pairs(CG/CG) by the DFT method, the lowest LUMO energy is 1.14 eV, and the energy levels of HOMO are between −2.08 ∼ −1.27 eV. In our study, The LUMO energy of the title complex is −2.966 eV, the energy of LUMO of the complex is lower than the energy of HOMO of DNA base-pairs and thus it suggests this complex is very excellent electron acceptors in their DNA-binding. Moreover, the good planarity of main-ligand of complex can contribute to intercalate the DNA-base-pairs. From Figure 5, we can see that the LUMO and LUMO+1 on the π-components of intercalative ligand(phenanthroline) are predominantly populated, the ancillary ligand (phenanthroline) is advantageous to improve the DNA-binding affinity of the complex. The theoretical studies indicate that the title complex may prone to bind with DNA in a partial intercalative mode.

## Conclusion

A new nickel(II) coordination complex with dibromotyrosine and 1,10-phenanthroline was successfully synthesized. Its structure was determined by X-ray single crystal diffraction. The crystal belongs to Orthorhombic, space group $P2_12_12$. $a$ = 12.9546(11) Å, $b$ = 14.9822 Å, $c$ = 9.9705 Å, $V$ = 1935.2 Å, $Z$ = 1, $F(000)$ = 1008, $S$ = 0.969, $\rho_{calcd}$ = 1.742 g·cm$^{-3}$, μ = 4.688 mm$^{-1}$, $R_1$=0.0529 and $wR_2$ = 0.0738. The Ni(II) is coordinated by six atoms, namely, two nitrogen toms and two carboxylic oxygen atoms from 3,5-dibromo-L-tyrosine, and two nitrogen atoms from 1,10-phenanthroline, forming a neutral 4N+2O complex. The molecules are connected by hydrogen bonds to form a three-dimensional network. Theoretical calculation was carried out by density functional theory (DFT) B3LYP method employing 6-31+G* basis set. Then some frontier molecular orbital energies were calculated, the results show that the title complex is stable and is prone to bind with DNA in a partial intercalative mode.

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