Synthesis and spectroscopic interpretations of Co(II), Ni(II) and Cu(II) deoxycholate complexes with molecular docking of COVID-19 protease

Moamen S. Refat, Safyah B. Bakare, Tariq A. Altalhi, Kehkashan Alam, Ghaferah H. Al-Hazmi

INTRODUCTION

Deoxycholic acid, commonly known as choline acid, and bile acid. Deoxycholic acid is a secondary bile acid, which is byproducts of intestinal bacteria. The two primary bile acids secreted by the liver are cholic acid and chenodeoxycholic acid. Deoxycholic acid is soluble in alcohol and acetic acid. When it is pure, it comes in the form of a white to yellowish-white crystalline powder. Deoxycholic acid has been used since its discovery in various fields of human medicine. Deoxycholic acid is used in the human body to emulsify fats for absorption in the intestine. It is licensed in some countries as an emulsifier in the food industry. It is us ed outside the body to prevent and dissolve gallstones. Deoxycholic acid is used in research as a mild detergent to isolate membrane-bound proteins. Sodium deoxycholate is often used as a biological cleanser to leach cells and dissolve cellular and membrane components. Sodium deoxycholate mixed with phosphatidylycholine, is used in mesotherapy injection to produce lipolysis, and has been used as an alternative to surgical excision in treating lipomas. Deoxycholates and bile acid derivatives, in general, are actively being studied as structures for inclusion in nanotechnology. They also found applications in microprinting as photoresist ingredients. They also found applications in microprinting as photoresist ingredients. They also found applications in microprinting as photoresist ingredients.

The carboxylate anion can adopt a wide range of bonding modes (monodentate symmetric and asymmetric chelating and bidentate and monodentate bridging)12. The literature survey of the past few years reveals the fact that a significant development in the field of biological activity of metal chelates plays a vital role in the case and treatment of cancer13-16. Metal complexes of carboxylic acids have been studied extensively17, 18, but there are not any works on complexes of deoxycholic acid. A clear understanding of the structure and spectroscopic properties of metal complexes usable for their biological applications is the aim of the present work. The present work deals with the synthesis and characterization of Co, Ni, and Cu(II) complexes of deoxycholic acid. Also, we aimed to study the interaction of COVID-19 protease (6LU7) by molecular docking studies, with all three complexes of deoxycholic acid with Co(II), Ni(II) and Cu(II). Furthermore, in the case of Co(II) deoxycholate complex, the probe is surrounded by amino residues Met235, Pro241, Gln240, Pro108, Glu110, Phe294, and Ile152. The probe molecule of Ni(II) deoxycholate complex is sited close to amino acids Tyr126, Tyr239, Leu287, Leu272, and Lys137. For, Cu(II) deoxycholate complex, the residues of amino acids comprise of Pro132, Pro108, Glu110, Gly109, Ile200, Asn203, Val202, His246, Pro293 and Tyr154. The binding energy was determined from the docking reads for Co(II)–6LU7, Ni(II)–6LU7 and Cu(II)–6LU7 deoxycholate compounds were found to be −446.99, −500.52, −398.13 kcal mol−1 individually.

Keywords: deoxycholic acid; complexes; ESR; TGA/DSC; molecular docking.
EXPERIMENTAL

Chemicals

Sodium deoxycholate and metal salts (CoCl₂ · 6H₂O, NiCl₂ · 6H₂O, and CuCl₂ · 2H₂O) were received from “Sigma–Aldrich Chemical Corporation, St. Louis, Mo, USA”. Synthesis of deoxycholate complexes

Co, Ni, and Cu(II) complexes of deoxycholate complexes were prepared by the same procedures, methanol 95% was employed as solvent. All the chemical reagents were of analytical grade and used without further purifications. CoCl₂ · 6H₂O, NiCl₂ · 6H₂O, and CuCl₂ · 2H₂O (1 mmol) were dissolved in 20 mL of methanol and then these solutions were slowly added to 30 mL of an aqueous solution with 2 mmol of sodium deoxycholate under a magnetic stirring. The reaction mixtures were refluxed at 65°C for two hours and left stand to evaporate slowly at room temperature overnight. The obtained solid precipitates were filtered off, wash with hot methanol solvent, dried at 80°C and then stored under vacuum over anhydrous phosphorus pentoxide.

Instrumentals

The carbon, hydrogen and nitrogen elements have been performed using Perkin Elmer CHN 2400. The determination of the percentages of metal ions was estimated based on the thermal gravimetric analysis technique. Melting points were carried out using MPS10–120 Melting point apparatus. FTIR spectra of the synthesized complexes were performed on Bruker FTIR Spectrophotometer. At room temperature with freshly prepared solutions, molar conductance of 10⁻³ M solutions in dimethyl sulfoxide (DMSO) solvent were measured using a Jenway 4010 conductivity meter. The electronic spectra were scanned in situ dimethyl sulfoxide within 200–800 nm range by UV2 Unicam UV/Vis Spectrophotometer. The effective magnetic moment (μ_eff) of the complexes was measured using Gouy’s method by the help of a magnetic susceptibility balance from Johnson Metthey and Sherwood model. The ESR spectrum of the diamagnetic copper(II) complex was scanned by a JES-FE2XG EPR Spectrometer. Thermogravimetric analysis (TGA) experiments were measured using TGA/DSC–50H Shimadzu analyzer. All experiments were performed using a single loose top-loading platinum sample pan under nitrogen atmosphere at a flow rate of 30 mL/min and a 10°C/min heating rate for the temperature range 25–800°C.

RESULTS AND DISCUSSION

Elemental analysis and conductance data

Analytical data of the Co, Ni, and Cu(II) deoxycholate complexes are summarized above in Table 1, and the results obtained are reliable with those calculated for the proposed formulae. All these complexes were stable at atmospheric conditions, non-hygroscopic, and soluble in organic solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The molar conductivity of the deoxycholate complexes in dimethyl sulfoxide (10⁻³ M) at 25°C is proportionate with their non-electrolytic nature (15–20 Ω⁻¹ cm² mol⁻¹). However, the analytical, spectroscopic, and magnetic data do enable us to predict the possible structure of the synthesized complexes.

Table 1. Microanalytical and physical analysis results for deoxycholate complexes

| Compounds | Color | Yield (%) | Conductance/Ω⁻¹ cm² mol⁻¹ | Analysis Found/Calcd % |
|-----------|-------|-----------|--------------------------|------------------------|
| [Co(C₂H₅O₂)₃·H₂O] · 4H₂O | Red | 65 | 20 | C: 60.54 (60.68) H: 9.43 (9.55) M: 6.09 (6.20) |
| [Ni(C₂H₅O₂)₂(H₂O)] · 4H₂O | Green | 68 | 15 | C: 60.33 (60.69) H: 9.21 (9.55) M: 6.11 (6.18) |
| [Cu(C₂H₅O₂)₂(H₂O)] · 2H₂O | Green | 71 | 18 | C: 62.70 (62.75) H: 9.39 (9.44) M: 6.88 (6.92) |

Table 2. Infrared spectral assignments of the deoxycholate complexes

| Sodium deoxycholate | Co(II) | Ni(II) | Cu(II) | Assignments |
|---------------------|--------|--------|--------|-------------|
| 3394                | 3373   | 3387   | 3415   | ν(OH) |
| 2935                | 2933   | 2933   | 2934   | ν₅(CH) |
| 2864                | 2864   | 2864   | 2864   | ν₅(CH) |
| 1566                | 1552   | 1542   | 1596   | ν₁₀(OCO) |
| 1449, 1406, 1302    | 1461, 1410, 1332, 1299 | 1420, 1376, 1301 | 1448, 1417, 1377, 1304 | δ(CH₂) + ν₁₀(OCO) |
| 1164                | 1206   | 1164   | 1090, 1038 | ν₆(CH₃) |
| 1093, 1040          | 1091, 1039 | 1090, 1038 | 1090, 1038 | ν₆(CC) |
| 945                 | 948    | 944    | 945    | ν₁₀(CC) |
| 917                 | 849, 805 | 880, 789 | 851     | δ(CC) + δ(OCO) |
| 614                 | 656, 615 | 710, 614 | 652, 615 | ν₁₀(OCO) + ν(M-O) |
difference between the asymmetric and symmetric carboxylato vibrations (Δν= v_{as}-v_{sym}) was calculated. The carboxylate group acts as a monodentate manner, when the difference between the v_{as}COO–v_{sym}CO is larger than ionic compounds. When the Δν is considerably smaller than the ionic compound, the carboxylate group coordinated towards metal ions as a bidentate fashion. In the spectra of the deoxycholate sodium salt and complexes, characteristic infrared bands arising from the frequencies of the carboxylate anion appeared. The stretching vibrations of the symmetric carboxylate anion v_{sym}(COO) are present at the wavenumbers 1566 cm⁻¹, 1552 cm⁻¹, 1542 cm⁻¹, and 1596 cm⁻¹ in deoxycholate sodium salt,²⁰ cobalt complex, nickel complex, and copper complex respectively, and the stretching asymmetric v_{as}(COO) at the wavenumbers 1302 cm⁻¹, 1332 cm⁻¹, 1376 cm⁻¹, and 1377 cm⁻¹ IR in deoxycholate sodium salt, cobalt complex, nickel complex, and copper complex respectively (Table 3). Based on the position of these bands in the sodium salt, it was found that the differences between the frequencies were determined as 264, 220, 166 and 219 for deoxycholate sodium salt, cobalt complex, nickel complex, and copper complex respectively. These results for Δν values indicated that the carboxylato group participates in a bidentate manner for the complexes (Fig. 1).

New vibration bands have been noticed in spectra of prepared complexes at wave number ranges 615 cm⁻¹ for the complexes (Fig. 1).

The electronic reflectance spectra of Co(II), Ni(II), and Cu(II) deoxycholate complexes were recorded in solid-state. The octahedral cobalt(II) complexes have a pink or reddish brown but most tetrahedral Co(II) complexes have an intense blue or green color, herein the electronic spectrum of the red color complex, [Co-(C_{24}H_{39}O_{4})_{2}(H_{2}O)_{2}] · 4H_{2}O, showed that this complex has an octahedral geometry. There are two electronic bands at 23529 cm⁻¹ and 28571 cm⁻¹ attributed to ^2T_{1g}→^4T_{2g} and ^2T_{1g}→^4T_{1g}(P) transitions, respectively. The magnetic moment of the cobalt(II) complex was found at 3.84 B.M. at room temperature which supported the octahedral geometry (Fig. 1). The electronic spectra of the synthesized nickel(II) exhibited two electronic absorption bands at 14970 and 29239 cm⁻¹ correspond to the ^3A_{2g}(F)→^3T_{1g}(F) (ν2) and ^3A_{2g}(F)→^3T_{1g}(P)(ν2) transitions respectively. These transitions revealed that the nickel(II) complex has an octahedral geometry.²ⁱ The effective magnetic moment value (μ_{eff}) of the Ni(II) complex was 3.20 BM. This value indicated that there were two unpaired electrons so that the complex was paramagnetic. The values of μ_{eff} 3.20 BM in the nickel complex indicated an octahedral complex²³. Hence, the Ni(II) complex was suspected to have octahedral geometry. The electronic spectrum of the green copper(II) complex, [Cu(C_{24}H_{39}O_{4})_{2}(H_{2}O)_{2}] · 2H_{2}O (Fig. 1) showed distinguish transition band at 20121 cm⁻¹ ascribe to ^2E→^2T_{2g} transition in a distorted octahedral geometry.²¹ The other absorption band at 28329 cm⁻¹ was assigned to L→M charge transfer. The found value of the magnetic moment of Cu(II) complex was 1.76 B.M., which supported the octahedral feature²¹.

X-band ESR spectrum of copper(II) complex, [Cu(C_{24}H_{39}O_{4})_{2}(H_{2}O)_{2}] · 2H_{2}O exhibited axial patterns of four lines due to the hyperfine coupling of the unpaired electrons with the copper nucleus (⁶³Cu, I = 3/2). The g and A values were calculated from the spectrum of the Cu(II) complex (Fig. 2). The trend g_{||} (2.1294) > g_⊥ (1.5971) observed in copper(II) complex indicate that the Cu(II) is in a distorted octahedral coordination environment, and the unpaired electron most likely resides predominantly in the d_{x^2–y^2} orbital of the Cu(II) ion and is the characteristic feature for the axial symmetry. The deviation of “g” values from the free-electron value (2.0023) is by angular momentum contribution in the complexes. The average “g” value for overall distortion is calculated using the equation: g_{av} (1.7745) = 1/3(2g_{||} + g_⊥)²⁴. Molecular orbital coefficients in-plane σ-bonding (α²), in-plane π-bonding (β²), and out-of-plane π-bonding (γ²) are the covalency parameters for the metal to ligand bond which were evaluated using the following expressions:

\[ \alpha^2 = (A_{11}/0.036) + (g_{||} - 2.0027) + 3/7 (g_⊥ - 2.0023) + 0.04) \]
\[ \beta^2 = (g_{||} - 2.0023)E / - 8\lambda\alpha^2 \]
\[ \gamma^2 = (g_⊥ - 2.0023)E / - 2\lambda\alpha^2 \]

where \( \lambda = -829 \) cm⁻¹ for the free copper ion and E is the electronic transition energy. The observed values of α² and β² indicate that the complex has covalent bonding character. The smaller the β², the larger the covalency of the bonding. Furthermore, it has appeared that the covalency of the out-of-plane is greater than of the in-plane π-bonding.

**UV-Vis spectra, ESR and magnetic susceptibility**

The electronic reflectance spectra of Co(II), Ni(II), and Cu(II) deoxycholate complexes were recorded in solid-state. The octahedral cobalt(II) complexes have a pink or reddish brown but most tetrahedral Co(II) complexes have an intense blue or green color, herein the electronic spectrum of the red color complex, [Co-

---

**Table 3. The stretching of asymmetric and symmetric vibrations of the carboxylate group**

| Compounds         | v_{as}(COO) | v_{sym}(COO) | Δν = v_{as} - v_{sym} | Bonding mode    |
|-------------------|-------------|--------------|------------------------|-----------------|
| sodium deoxycholate | 1566       | 1302         | 264                    | Bidentate       |
| Co(II)            | 1552       | 1332         | 220                    | Bidentate       |
| Ni(II)            | 1542       | 1376         | 166                    | Bidentate       |
| Cu(II)            | 1596       | 1377         | 219                    | Bidentate       |
Thermal analysis

The TG/DSC study for the \([\text{Co(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}, \text{[Ni(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) and \([\text{Cu(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 2\text{H}_{2}\text{O}\) deoxycholate complexes are assigned and listed in Table 4 and the thermal diagrams are shown in Fig. 3a–c. The final solid products as a residual that is associated with the thermal decompositions of deoxycholate complexes are CoO, NiO and CuO.

The TGA/DSC curves of the cobalt(II) complex show four endothermic peaks at (71, 428, 496, and 621°C) and three exothermic peaks at (710, 745, and 771°C) with a total mass loss 93% (calcd. 92.11%) corresponds to the release of two deoxycholate (C_{24}H_{39}O_{4}), six coordinated and uncoordinated water molecules. Hence, the cobalt(II) deoxycholate complex decomposes to cobalt oxide (CoO) with intermediate formation of cobalt carbonate (see Fig. 3a). The two \([\text{Ni(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) and \([\text{Cu(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 2\text{H}_{2}\text{O}\) deoxycholate complexes are stable up to 100°C with DSC maximum peaks at (110°C, 320°C, 498°C, and 690°C) and (100°C, 327°C, 430°C, and 585°C) respectively, and then lose the two deoxycholate molecules in three decomposition steps (Figs. 3b&c) over 100–700°C. The anhydrous two complexes decompose to metal carbonate form as an intermediate over 300°C and the last one with the formation of NiO and CoO oxides.

It is evident that different complexes of sodium deoxycholate with Co(II), Ni(II) and Cu(II) may have a unique impact on COVID-19 protease. However, it is hard to decide the differences through the experiments. Henceforth, to determine the difference, a computational study could be utilized\(^{25,26}\). So, the molecular docking was performed

Table 4. Main TGA and DSC data for the deoxycholate complexes

| Complexes | DSC | Mass loss (%) Found (Calc.) | Losses molecules | Residue products |
|-----------|-----|-----------------------------|-----------------|-----------------|
| \([\text{Co(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) | 71 endo, 428 endo, 496 endo, 621 endo, 710 exo, 745 exo, 771 exo | 30–100, 500–600, 600–700, 700–730, 730–760, 760–800 | 93(92.11) | 2(C_{24}H_{39}O_{4}) \cdot 6H_{2}O | CoO |
| \([\text{Ni(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) | 110 endo, 320 endo, 498 endo, 690 exo | 30–120, 120–400, 400–500, 600–800 | 92.50(92.14) | 2(C_{24}H_{39}O_{4}) \cdot 8H_{2}O | NiO |
| \([\text{Cu(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 2\text{H}_{2}\text{O}\) | 100 endo, 320 endo, 498 endo, 690 exo | 30–150, 150–400, 600, 800–600 | 91(91.34) | 2(C_{24}H_{39}O_{4}) \cdot 4H_{2}O | CuO |

Figure 2. ESR spectrum of copper (II) deoxycholate complex

Figure 3. a) TGA and DSC curves of \([\text{Co(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) complex; b) TGA and DSC curves of \([\text{Ni(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 4\text{H}_{2}\text{O}\) complex; c) TGA and DSC curves of \([\text{Cu(C}_{24}\text{H}_{39}\text{O}_{4})_{2}(\text{H}_{2}\text{O})_{2}] \cdot 2\text{H}_{2}\text{O}\) complex
to identify the interaction of 6LU7 with Co(II), Ni (II) and Cu(II) deoxycholate complexes. The most possible docking pose between 6LU7 and different complexes of sodium deoxycholate and related data are shown in Table 5, 6 and Fig. 4–6. The binding sites of prepared complexes show that interactions are considerably different in each case as represented from Fig. 4–6. In the case of Co(II) deoxycholate complex, the probe molecule is bounded by amino acid residues Met235, Pro241, Glu240, Pro108, Gln110, Phe294, Ile152. The probe molecule of Ni(II) deoxycholate complex is sited next to amino acid residues Tyr126, Tyr239, Leu287, Leu272, and Lys137. For, Cu(II) deoxycholate complex, the amino acid residue consists of Pro132, Pro108, Gln110, Gly109, Ile200, Asn203, Val202, His246, Pro293, Tyr154. In addition, four hydrogen bonds are observed in Co(II), Ni(II) complex while five hydrogen bonds are found in the case of Cu(II) deoxycholate complex and other details are summarized in Table 6. The value of binding energy was calculated from the docking studies for Co(II)–6LU7, Ni(II)–6LU7 and Cu(II)–6LU7 deoxycholate complexes were $-446.99$, $-500.52$, $-398.13$ kcal mol$^{-1}$ respectively. The binding affinity of Co(II)–COVID-19 protease was found to be $-446.99$ kcal mol$^{-1}$ indicating the slightly higher binding energy than Cu(II)–6LU7 and slightly lower than Ni(II)–6LU7. The estimated inhibition

![Figure 4. Molecular docking pose of the Co(II) complex with COVID-19 protease (6LU7) (a) Showing interaction with amino acids (b) surface showing hydrogen bond interaction](image)

![Figure 5. Molecular docking pose of the Ni (II) complex with COVID-19 protease (6LU7); (a) Showing interaction with amino acids; (b) surface showing hydrogen bond interaction](image)

![Figure 6. Molecular docking pose of the Cu(II) complex with COVID-19 protease (6LU7) (a) Showing interaction with amino acids (b) surface showing hydrogen bond interaction](image)

| Complexes          | Residue | Amino Acid | Distance H-A | A (Acceptor atom) | Interacting amino acids |
|--------------------|---------|------------|--------------|-------------------|------------------------|
| Co(II) deoxycholate complex | 108A | Pro | 2.11 | O$_2$ | Met235, Pro241, Glu240, Pro108, Gln110, Phe294, Ile152 |
|                    | 110A    | Gln        | 3.10         | O$_2$          |                        |
|                    | 153A    | Asp        | 3.20         | O$_2$          |                        |
|                    | 241A    | Pro        | 2.61         | O$_2$          |                        |
| Ni(II) deoxycholate complex | 131A | Arg        | 3.44         | O$_3$          |                        |
|                    | 131A    | Leu        | 3.86         | O$_3$          |                        |
|                    | 287A    | Asp        | 3.02         | O$_3$          |                        |
|                    | 289A    | Asp        | 3.02         | O$_3$          |                        |
| Cu(II) deoxycholate complex | 109A | Gly        | 2.56         | O$_3$          |                        |
|                    | 110A    | Gln        | 2.12         | O$_3$          |                        |
|                    | 198A    | Thr        | 2.45         | O$_3$          |                        |
|                    | 292A    | Thr        | 3.26         | O$_3$          |                        |
|                    | 294A    | Phe        | 1.62         | O$_3$          |                        |

Table 6. Hydrogen bond interactions

Table 5. The docking interactions parameters
Constant, $K_i$ is 48.39 mM (millimolar) which is found in the case of Cu(II) complex. So, this complex has a higher ability to inhibit the biological process of target COVID-19 protease (6LU7).

**CONCLUSION**

The synthesis of the complexes between sodium deoxycholate and essential metal ions (Co(II), Ni(II) and Cu(II)) were studied to investigate the complexation behavior of these systems as it could mimic many biological interactions. The complexes appear to be superior in biological properties dependent on the molecular docking that utilizing to additionally examine the interaction of COVID-19 (6LU7). The complete elucidation molecular structures of the synthesized deoxycholate complexes were confirmed by detailed microanalytical ‘elemental analysis’, molar conductivity, (infrared and Raman) spectroscopy, thermal analyses (TGA/DSC), UV-vis spectra, and ESR techniques. The spectroscopic analysis of the complexes shows that deoxycholate molecule acts as a bidentate ligand with octahedral geometry.

**ACKNOWLEDGMENT**

Taif University Researches Supporting Project number (TURSP-2020/01), Taif University, Taif, Saudi Arabia.

**LITERATURE CITED**

1. Lide, D.R. (1998). *Handbook of Chemistry and Physics*. (87 ed.). Boca Raton, FL: CRC Press. p. 1287.
2. Streuli, H. (1992). SLMB – Schweizer Lebensmittelbuch, chapter 58, 4/3.
3. Neugebauer, J.M. (1990). “Detergents: An Overview” in M.P. Deutscher, Guide to Protein Purification (Methods in Enzymology Vol. 182), Academic Press, San Diego. DOI: 10.1016/0076-6879(90)82020-3.
4. Duncan, D. & Rotunda, A.M. (2011). Injectable therapies for localized fat loss: state of the art. *Clin. Plast. Surg.*, 38(3), 489–501, DOI: 10.1016/j.cps.2011.02.005.
5. Kim, J.B., Lee, B.W. , Yun, H.J. & Kwon, Y.G. (2000). 193-nm Photoresists Based on Norbornene Copolymers with 489–501, DOI: 10.1016/j.cps.2011.02.005.
6. Tejam, A.B. & Thakkar, N. (1997). Extractive spectrophotometric determination of Co(II) at trace level using l-phenyl 1,2-propanediol dioxime. *Indian J. Chem.*, 36(A), 1008–1009.
7. Bhai, S. & Ganguly, B. (2019). Role of backbones on the interaction of metal ions with deoxyribonucleic acid and peptide nucleic acid: A DFT study. *J. Mol. Graph. Model.*, 93, 107445. DOI: 10.1016/j.jmgm.2019.107445.
8. Murphy, J.M., Powell, B.A. & Brumaghim, J.L. (2020). Stability constants of bio-relevant, redox-active metals with amino acids: The challenges of weakly binding ligands. *Coord. Chem. Rev.*, 412, 213253. DOI: 10.1016/j.ccr.2020.213253.
9. Deacon, G.B. & Phillips, R.J. (1980). Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. *Coord. Chem. Rev.*, 33, 227–250. DOI: 10.1016/S0010-8545(00)80455-5.
10. Khan, I.M., Alam, K., Alam, M.J. & Ahmad, M. (2019). Spectrophotometric and photocatalytic studies of H-bonded charge transfer complex of oxalic acid with imidazole: single crystal XRD, experimental and DFT/TD-DFT studies. *New J. Chem.*, 43, 9039–9051. DOI: 10.1039/C9NJ00332K.
11. Nakamoto, K. (1997). *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York.
12. Lever, A.B.P. (1997). *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam.
13. Craig, G.A., Sarkar, A., Woodall, C.H., Hay, M.A., Marriot, K.E., Kamenev, K.V ., Moggach, S.A., Brechin, E.K., Parsons, S., Rajaraman, G. & Murrie, M. (2018). Probing the origin of the giant magnetic anisotropy in trigonal bipyramidal Ni(II) under high pressure. *Chem. Sci.*, 9, 1551–1559. DOI: 10.1039/ C7SC04460G.
14. Omaka, N.O., Ekennia, A.C., Njoku, N.N. & Onwudike, D.C. (2018). Nickel(II) and copper(II) complexes of 2,2′-bibenzo[d]thiazole: Synthesis, characterisation and studies. *App. Organsom. Chem.*, 32(4), e4241, DOI: 10.1002/aoc.4241.
15. Vernale, N.G. & Mruthunjayawamy, B.H.M. (2014). Antibacterial and Anti-Inflammatory Activities of New Schiff Base Ligand Derived from Thiazole and Quinoline Moiety. *Bioinorg. Chem. Appl.*, 2014, Article ID 314963, 17. DOI: 10.1155/2014/314963.
16. Zhang, F., Zhang, J., Tong, C.L., Chen, Y.D., Zhuang, S.L . & Liu, W.P . (2013). Molecular interactions of benzophenone UV filters with human serum albumin revealed by spectroscopic techniques and molecular modeling. *J. Hazard. Mater.*, 263, 618–626. DOI: 10.1016/j.jhazmat.2013.10.024.
17. Elgawish, M.S., Kishikawa, N., Helal, M.A., Ohyama, K. & Kuroda, N. (2015). Molecular modeling and spectroscopic study of quinone–protein adducts: insight into toxicity, selectivity, and reversibility. *Toxicol. Res.*, 4, 843–847. DOI: 10.1039/c6tx000998.
18. Mumin, M.A., Pal, T.K., Alam, M.A., Islam, M.A., Paul, S. & Sheikh, M.C. (2020). DFT studies on vibrational and electronic spectra, HOMO–LUMO, MEP, HOMA, NBO and molecular docking analysis of benzyl-3-N-(2,4,5-trimethoxy-phenylmethylene)hydrazinocarbodithioate. *J. Mol. Struct.*, 1220, 128715. DOI: 10.1016/j.molstruc.2020.128715.