RESEARCH PAPER

Synthesis, Characterization, and Antibacterial Activity of Ni(II), Pd(II), and Pt(II) Complexes with 2-benzoylthiobenzimidazole

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A B S T R A C T:

The thioester compound of 2-benzoylthiobenzimidazole was prepared by S-acylation of 2-mercaptopbenzimidazole with benzoyl chloride and reactions of divalent Ni, Pd, and Pt salts with one equivalent of thioester compound a new complexes were isolated in a high percentage. A tetradeentate thioester compound and a bivalent metal complexes were identified by CHNS analysis, IR, magnetic susceptibility, molar conductivity, UV-Vis, and ¹H, ¹³C NMR spectroscopies. The anti-bacterial activity of the thioester compound and the bivalent metal complexes were studied using disk diffusion test method against the bacterial species, Staphylococcus aureus, and Pseudomonas aeruginosa. The divalent metal complexes demonstrated a greater activities compared to thioester compound alone. Structural analysis showed that 2-benzoylthiobenzimidazole L behaves as a neutral four coordination modes compound and bonds to the bivalent metals cation through two nitrogen, sulfur and oxygen atoms. Our study informed the formation of four-coordinate square planar complexes structure around divalent metal salts of Ni, Pd, and Pt.

KEY WORDS: 2-benzoylthiobenzimidazole; Square planar geometry; Divalent metal ions complexes; Antibacterial activity, Structural study.

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INTRODUCTION:

Transition coordination compounds were analyzed and get more significant in coordination chemistry for a numerous analyst around the world since of their molecular structure bind together by the interactions in a single structure, such as acid to base interaction, metal to ligand and ligand to metal charge transfer (Steed and Atwood, 2000; Sauvage, 1999). Inorganic compounds and coordination chemistry have been comprehensively used in catalysts, drug chemistry and biochemical application (Gupta and Sutar, 2008). Derivatives of 2-benzimidazolethiol are a significant part of heterocyclic chemistry as a result of their extensive play in biochemical and pharmaceutical studies such as antibacterial (Mavrova et al., 2010), antimicrobial (Gurrala et al., 2011) antitubercular (Gupta and Pancholi, 2011), antifungal (Huang et al., 2007), antagonist and antihistamine (Okamoto et al., 2008). Thioester consisting of heterocyclic compound one of the most essential organosulfur compounds that are the main constituent of biological ester and pharmaceutical compounds (Neumann and Walsh, 2008; Schwarzer et al., 2011). Thiol derivatives reacts with acyl chloride one of the

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significant method for the preparation of heterocyclic thioester compounds (Kazemi and Shiri, 2015). The acylation of a sulfur atom of heterocyclic thiols (S-acylation) gives a sufficient and competitive way to keep SH group in the preparation progress (Ko et al., 2006; Goux et al., 1994). Thioester compounds have been effectively used as a raw material for the synthesis of a new drug, and cosmetic. Mixed ligand complexes of thioester compounds with tertiarydiphosphine ligand were also been identified and published (Ali et al., 2017). In this study, the newly thioester ligand have been currently prepared by the S-acylation of 2-benzimidazolethiol with benzoyl chloride. In this report, a newly three bivalent metal complexes of this ligand were investigated, and these complexes showed a significant activity against the P. aeruginosa and S. aureus bacteria.

1. MATERIALS AND INSTRUMENTATION

Anhydrous divalent, palladium and platinum salt and 2-benzimidazolethiol was achieved and obtained from Suzhou Yacoo Science Co. NiCl$_2$.6H$_2$O from Sigma Aldrich Company. All solvents were brought from Sigma Aldrich. Elemental investigation was taken by a EURUEA 300 CHNS analyzer. FTIR Shimadzu 8400S spectrophotometer was used by using CsI disc and KBr discs from 4000-200 cm$^{-1}$ and 4000-400 cm$^{-1}$ respectively. Burkeir 400 MHz spectrometer was used to record $^1$H and $^{13}$C NMR spectra in CDCl$_3$ as solvent and TMS as an internal standard. AE-UV1609 (UK) CO., LTD Shimadzu spectrometer was used to measure UV-Vis spectra using a chloroform solvent. Magnetic moment of synthesized transition compounds was measured at 25 °C on Johnson Brukeir Magnet BM6. Digital Senz mSiemen conductivity meter was used on 10$^3$M solution to measure conductivity of complexes. MPD-200 pixel Melting point, apparatus was used to record melting point of prepared compounds.

1.1 2-benzoylthiobiobenzimidazole

A mixture of 2-benzimidazolethiol (9.02g, 0.06 mol) and potassium carbonate (8.3g, 0.06 mol) was added to acetone (125ml) in distilling flask (250ml) and then the solution mixture was for about 10 min after that added benzoyl chloride (8.434g, 0.06mole) by droops and refluxed for another 4 hr., left a mixture to cool at room temperature and add 100 ml of water, and acidified with dilute acetic acid, then isolate product and rinse by water several times. Yield: 11.296 g (74%), m.p.: (197 °C). M.Wt: 254.307 g/mol. IR spectrum: 3057 (Ar), 1618 (CN), 1712 (CO), 3151 (N-H), 657 (C=S), 1350 (C-N). UV-Vis spectrum, $\lambda_{max}$, nm: 238.8, 307.8 and 383. $^1$H NMR spectrum, $\delta$, ppm: 10.72 s (1H, NH), 7.26-7.52 (2H, Ar), 7.42-7.91 d (2H, Ar), 7.69 t (1H, Ar).$^{13}$C NMR spectrum, $\delta$C, ppm: 169.18 (C=O), 109.95 (C9, Ph), 112.67 (C10, Ph), 124.02 (C11, Ph), 125.11 (C3, Ph), 128.86 (C4, Ph), 130.87 (C5, Ph), 131.04 (C2, Ph), 132.20 (C8, Ph), 132.71 (C7, Ph), 134.5 (C6, Ph), 169.18 (C1, Ph).

1.2 Synthesis of the complexes

In general manner, Bivalent metal complexes were synthesized by add NiCl$_2$.6H$_2$O, PdCl$_2$ and PtCl$_2$ (2.0 mmol) in methanol (20 mL) to the 2-benzoylthiobiobenzimidazole ligand (1 mmol) in methanol (20 mL). The resulting mixtures were refluxed for 4 h., allow the mixtures to evaporate at room temperature and purified the product by washing three times with diethyl ether.

[Ni$_2$LCl$_4$].2H$_2$O: yellow green solid, yield 82%, mp 166°C, M.Wt: 419.96 g/mol.. IR spectrum: 3381 (OH), 3163 (NH), 3052 (CH)$_2$, 1612 (CN), 1691(CO), 482 (Ni-O), 582 (Ni-Cl), UV–Vis spectrum, $\lambda_{max}$ nm: 254, 310, and 524.

[Pd$_2$LCl$_4$]: Orange brown solid, yield 73%, mp 292°C, M.Wt: 609.14 g/mol. IR spectrum: 3162 (NH), 3056 (CH)$_2$, 1616 (CN), 1701(CO), 507 (Pd-N), 553 (Pd-NH), 451 (Pd-S), 470 (Pd-O), 343 (Pd-Cl). UV–Vis spectrum, $\lambda_{max}$, nm: 248, 350, and 426.

[Pt$_2$LCl$_4$]: Brown yellow solid, yield 72%, mp >310°C, M.Wt: 786.46 g/mol. IR spectrum: 3159 (NH), 3059 (CH)$_2$, 1608 (CN), 1699 (CO), 514 (Pd-N), 534 (Pd-NH), 443 (Pd-S), 472 (Pd-O), 337 (Pd-Cl). UV–Vis spectrum, $\lambda_{max}$, nm: 256, 308, and 435.

1.3 Bacterial species

In the study we used one gram negative bacterium and one gram positive bacterium. The standard strains of the following microorganism were used as test organisms: Pseudomonas aeruginosa (ATCC15442) and Staphylococcus aureus (MTCC1144).

2. RESULTS AND DISCUSSION

Physical properties and analysis data of 2-benzoylthiobiobenzimidazole and bivalent
coordination compounds are collected in the Table 1. A new 2-benzyliothiolbenzimidazole ligand was synthesized by the esterification of thiol 2-mercaptobenzimidazole with benzoyl chloride 1:1 M ratio in acetone (Scheme 1) (Heralagi, et al., 2012). A 2-benzyliothiolbenzimidazole have four donor atoms (O, 2N, S) that capable to the formation of binuclear bivalent metal complexes. Spectroscopic studies and CHNS analysis data showed that the complexes structures are [Ni2LCl4].2H2O and [M2LCl4] (where M= Pd(II), Pt(II) and L= 2-benzyliothiolbenzimidazole ligand).

An expected complexes structures are comparable with data taken by spectroscopic techniques, magnetic moment and molar conductivity. The conductivity value of bivalent nickel, palladium, and platinum complexes in dimethyl sulfoxide (DMSO) were 17.3, 12 and 10.6 (mol\(^{-1}\).cm\(^2\).ohm\(^{-1}\)) that declares the complexes are nonelectrolyte since all chloride atoms is coordinated to bivalent metal ions and no chlorine is present outside the coordination sphere. A complexes expected structure is in the (Scheme 2).

### Table 1. Analytical and physical data of the ligand and their complexes

| Compound | m.p °C | µₜₜ, BM | Colour            | Analysis found (calculated), % | Ω\(^{-1}\) mol\(^{-1}\) cm\(^2\) |
|----------|--------|---------|-------------------|--------------------------------|----------------------------------|
| [L] \(\text{C}_{14}\text{H}_{10}\text{N}_{2}\text{O}_{2}\text{S}\) | 197    |         | light yellow      | C: 66.31 (66.12) H: 3.86 (3.96) N: 11.11 (11.02) S: 12.70 (12.61) | 4.8                             |
| \(\text{C}_{14}\text{H}_{10}\text{N}_{2}\text{OSN}_{2}\text{Cl}_{4}\) | 166    | 0.48    | yellow green      | C: 40.00 (39.73) H: 3.43 (3.39) N: 6.66 (6.57) S: 7.62 (7.94) | 17.3                            |
| \(\text{C}_{14}\text{H}_{10}\text{N}_{2}\text{OSP}_{2}\text{Cl}_{4}\) | 292    | 0.34    | orange brown      | C: 27.42 (27.57) H: 1.53 (1.64) N: 4.53 (4.59) S: 5.23 (5.25) | 12                              |
| \(\text{C}_{14}\text{H}_{10}\text{N}_{2}\text{OSP}_{3}\text{Cl}_{4}\) | >310   | 0.38    | Brown yellow      | C: 22.09 (21.36) H: 1.24 (1.27) N: 3.46 (3.56) S: 4.11 (4.06) | 10.6                            |

**Scheme 1. Synthesis of the 2-benzyliothiolbenzimidazole ligand.**
2.1 The IR Spectra

Table 2 shows many bands of 2-benzoylethiobenzimidazole ligand and its bivalent metal complexes. In the IR spectrum of thioester ligand the strong absorption peak at 1712 cm\(^{-1}\) due to the ν(C=O) carbonyl group (Rao, et al., 2013; Awaz, 2015). In the Ni(II), Pd(II), and Pt(II) complexes, the strong band of ν(C=O) carbonyl groups shifted to the lower frequency to 1691, 1701 and 1699 cm\(^{-1}\) respectively, by complexation through carbonyl Oxygen to metal atoms (Uçan, 2014). The ligand showed a strong band at 1618 cm\(^{-1}\) related to ν(C=N) azomethine group (Hamad, et al., 2016), and the strong peaks at 1612, 1616 and 1608 cm\(^{-1}\) attributed to ν(C=N) azomethine group in the bivalent Ni, Pd, and Pt complexes respectively after complexation through the nitrogen of azomethine group (Pessoa, et al., 1998). In addition, the new broad peaks at 3350 cm\(^{-1}\) contributed to uncoordinated water molecules was appeared in the Ni(II) complex with the ligand (Al-Jibori, et al., 2002). Also, The bands at 560, 514, and 507 cm\(^{-1}\) due to ν(M-N) and the bands at 428, 482, and 470 cm\(^{-1}\) related to ν(M-O) have been appeared in the Ni, Pd and Pt complexes respectively (Amin, et al., 2004; Apenysheva, et al., 2006). A new ν(M-S) have been observed at 482, 451, and 443 cm\(^{-1}\) in the Ni, Pd, and Pt complexes respectively (Matin and Khojasteh, 2015). Similarly, new ν(M-NH) bands at 560, 553, and 534 cm\(^{-1}\) have been created in the Ni, Pd, and Pt complexes respectively (Khan, et al., 2000). In the complexes the bands at 368, 349 and 343 cm\(^{-1}\) belong to metal-halogen (M-Cl) coordination (Buttrus, et al., 2003).

**Table 2.** IR spectral data of the thioester ligand and its complexes.

| Compounds              | ν (OH) | ν (N-H) | ν (C=N) | ν (C=O) | ν (M-NH) | ν (M-N) | ν (M-S) | ν (M-O) | ν (M-Cl) |
|------------------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| [L] C\(_{14}\)H\(_{10}\)N\(_2\)OS | 3350   | 3159    | 1608    | 1699    | 534     | 507     | 443     | 470     | 343     |
| C\(_{14}\)H\(_{10}\)N\(_2\)OSNi\(_2\)Cl\(_4\) | 3161   | 1612    | 1701    | 553     | 514     | 451     | 482     | 482     | 349     |
| C\(_{14}\)H\(_{10}\)N\(_2\)OSPd\(_2\)Cl\(_4\) | 3161   | 1612    | 1701    | 553     | 514     | 451     | 482     | 482     | 349     |
| C\(_{14}\)H\(_{10}\)N\(_2\)OSPt\(_2\)Cl\(_4\) | 3159   | 1608    | 1699    | 534     | 507     | 443     | 470     | 470     | 343     |
2.2 The NMR spectra

Figure 1 and 2 displays the $^1$H and $^{13}$C NMR signals of thioester ligand. A $^1$H NMR. Showed singlet signal at 10.72 ppm for one proton attached to the (N-H) group (Ceylan, et al., 2017). The protons of benzene ring connected to the carbonyl group appeared at 7.91 ppm (2d, 2H), 7.52 ppm (t, 2H) and 7.68 ppm (t, 1H). The protons of 2-benzimidazolethiol ring showed a (d, 2H) at 7.42 ppm, (t, 2H) at 7.27 ppm (Kotovskaya, et al., 2001). The structure of the thioester ligand was evaluated further using $^{13}$C NMR that exhibited signal at 169.18 ppm corresponding to the carbon of (C=O) group (Farouq, 2018). The ligand also displayed signals at 109.95, 112.67, 124.02, 125.11, 128.86, 130.87, 131.04, 132.20, 132.71 and 134.5 ppm. The formation of these signals is a good confirmation for the thioester ligand formation (Karaoglu, et al., 2009).

![Figure 1. $^1$H-NMR spectrum of 2-benzoylthiobenzimidazole ligand](image1)

![Figure 2. $^{13}$C-NMR spectrum of 2-benzoylthiobenzimidazole ligand](image2)
2.3 Magnetic and conductivity study

Table 1 displays the value of magnetic susceptibility that carry out at 25°C. The values of magnetic susceptibility are of 0.48, 0.34, and 0.38 BM for the Ni, Pd, and Pt binuclear metal complexes respectively. These values of magnetic moment are in agreement with the formation of diamagnetic metal complexes (Ferenc, et al., 2018). The conductivity study of the metal complexes was measured in DMSO for 10^{-3} M at 25°C. The values of molar conductance was 17.3, 12.0, and 10.6 cm^2.ohm^{-1}.mol^{-1} for Ni, Pd, and Pt complexes respectively. The values of electrical conductivity indicated that the binuclear metal complexes are non-electrolytic since chlorine atoms are coordinated to the metal ions and no one outside the coordination sphere (Geary, 1971) (Table 1).

2.4 UV-Vis study

Figure 3 shows the UV-Vis peaks of the 2-benzoylthiobenzimidazole ligand and its binuclear metal complexes which measured in CHCl_3 in the range 200–800 nm. The carbonyl group of the thioester ligand showed a peak at 238.8, 307.8 nm and imidazole ring nitrogen has peaks at 348.8, 383 nm assigned to \( \pi \) to \( \pi^* \) (Aziz, et al., 2012) and \( n \) to \( \pi^* \) transition (Buyukuslu, et al., 2010). The \([\text{Ni}_2\text{LCl}_4]\).2H_2O complex displays, peaks at 19083, 32258, and 39370 cm^{-1} a first one was related to \( {}^1A_g \) to \( {}^1A_{2g} \) transition and the other two peaks were contributed to MLC transfer transition (Mihalache, et al., 2018). The \([\text{Pd}_2\text{LCl}_4]\) complex have bands at 23474, 28571 and 40322 cm^{-1} which were attributed to \( {}^1A_{1g} \) to \( {}^1B_{1g} \), \( {}^1A_{1g} \) to \( 1E_g \), and charge transfer transition respectively (Howlader, et al., 2019). The \([\text{Pt}_2\text{LCl}_4]\) complex shows bands at 22988, 32467 and 39062 cm^{-1}, the first one peak was referred to \( {}^1A_{1g} \rightarrow {}^1B_{1g} \) and the other two peaks which were indicated C.T transition (Alsalihi, et al., 2017).

Figure 3. UV-Vis spectra of ligand (L) and (Ni(II), Pd(II), Pt(II) complexes.
2.5 Biological activity

The antibacterial properties of ligand 2-benzoylthiobenzimidazole and its divalent metal complexes was measured on two kinds of bacteria *Pseudomonas aeruginosa* and *Staphylococcus aureus* by using an inhibition technique according to the literature (De Graaf et al., 2013; Ramezan et al., 2012). Figure 4 and table 3 illustrates the inhibition zone in (mm) against bacterial for one day. It is clear from the results that the binuclear metal complexes have more biological activity than the thioester ligand itself under the same condition. The chelation theory can answer the enhancement of the biological activity of coordination compounds (Bermejo et al., 1999). The ligands increased their biological activity and growth their inhibition area due to chelation in complexes than free ligand. The [Ni_2LCl_4].2H_2O complex has a high activity against the two types of bacteria compared to Pd and Pt complexes. The results of [Pt_2LCl_4] complex displaced remarkable activity for both microorganisms. The nickel and platinum complexes have high activity against *P. aeruginosa* and *S. aureus* microorganisms in contrast to [Pd_2LCl_4] complex.

### Table 3. Antibacterial activity results of ligand and its metal complexes

| Compound | Growth Inhibition zone against Bacteria In (mm) |
|----------|-------------------------------------------------|
|          | *P. aeruginosa* | *S. aureus* |
| KBr      | 0               | 0           |
| Ligand (L)| 5               | 4           |
| [Ni_2(L)Cl_4].2H_2O | 29             | 23          |
| [Pd_2(L)Cl_4]   | 15             | 12          |
| [Pt_2(L)Cl_4]   | 26             | 24          |

**Figure 4.** Antibacterial activity of the ligand and complexes

3. CONCLUSIONS

This research has shown the 2-benzoylthiobenzimidazole that contain imidazole group forms binuclear Ni(II), Pd(II) and Pt(II) complexes and these complexes were investigated by spectroscopic and analytical methods. The compound, 2-benzoylthiobenzimidazole was acting as tetradeinate ligand in the formation of binuclear metal ion complexes. The magnetic data showed that the bivalent metal complexes of thioester ligand are diamagnetic. The complexes of, 2-benzoylthiobenzimidazole have a good activity against microorganism *P. aeruginosa* and *S. aureus.*
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Conflict of Interest
There is no conflict of interest

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