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An eco-friendly synthesis, spectral characterization and biological significance of Ni(II) complex with 2,4-Thiazolidinedione and Benzoate ion as ligands

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Abstract

Abstract
The present work deals with synthesis of Ni(II) complex with the mixed ligands 2,4-thiazolidinedione and benzoate ion in an eco-friendly conditions utilizing microwave energy. The synthesized Ni(II) complex have been characterized by elemental analysis, metal estimation, molar conductance, magnetic moment, UV-Visible and FT-IR spectral techniques and also evaluated for anti-antibacterial, antifungal and antioxidant activities. The molar conductance value indicates that the Ni(II) complex is a non-electrolyte. The magnetic moment and UV-Visible spectrum indicates octahedral arrangement around Ni(II) ion. FT-IR spectra show that 2,4-thiazolidinedione and benzoate ion are coordinated to the metal ion in a monodentate way. The synthesized Ni(II) complex was found to possess good anti-bacterial, , anti- fungal and antioxidant activity than the ligands.

Keywords: *Microwave synthesis, 2,4-thiazolidinedione, benzoate ion, antioxidant*.

1. Introduction

Metal complexes of sulphur, oxygen and nitrogen containing have been reported for their antimicrobial activities [1,2]. The 2,4-thiazolidinedione is also contain sulphur, oxygen and nitrogen. It is a biolologically imperative class of heterocyclic compounds used for the treatment of type-2 diabetes [3-5]. The 2,4-thiazolidinedione and its derivatives lower the plasma glucose levels by acting as ligands for γ-peroxyzome proliferators-activated receptors [6,7]. Besides, this class of heterocyclic compounds possesses various other biological behavior such as antihyperglycemic, antimicrobial, anti-inflammatory, anticonvulsant and insecticidal, etc., [8, 9]. TLDs are also known for lowering the blood pressure and thereby reducing the chances of heart failure and micro-albuminuria in patients with type-2 diabetes [10,13]. A survey of literature reveals that the metal complexes of many drugs have been found to be more effective than the drug itself. Therefore, much attention is given to the use of TLD due to its high complexing nature with essential metals [13, 15].

The present study aims at the synthesis and spectral characterization of Ni(II) complex with 2,4 - thiazolidinedione and benzoate ion ligands. The ligands and their complex are then tested for antioxidant and antimicrobial activities.

2. Experimental

2.1. Materials and methods

Nickel nitrate, 2,4-thiazolidinedione and sodium benzoate were purchased from Alfa Aaser Company and used as such. The organic solvents used, viz., DMSO, DMF, methanol and ethanol were

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of AnalaR grade and used as such without further purification.

2.2. Synthesis of Ni(II) complex

1.66 g (13.79 mmol) of 2,4-thiazolidinedione in methanol and 1.00g (7.00 mmol) of sodium benzoate in ethanol were added to the nickel nitrate 1.00g (3.43 mmol) in methanol and this was followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The resulting precipitate was filtered off, washed with 1:1 ethanol: water mixture and dried under vacuum. A pale green colored complex was obtained with the yield of 65.9%.

2.3. Instrumentations

CHN elemental analyses were performed using Thermo Finnegan make, Flash EA1112 Series CHNS (O) analyzer. The electrical conductivity measurements were conducted using 10-3 M solutions of the metal complex in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV-Visible spectrum of the Ni(II) complex was recorded on Varian, Cary 5000 model UV-Vis Spectrophotometer. FT-IR spectra for the complex and the free ligands were recorded on a Perkin Elmer, Spectrum RX-I, FT-IR Spectrometer in KBr discs at room temperature.

3. Biological studies

3.1. Antimicrobial activity

The free ligands 2,4-thiazolidinedione, sodium benzoate and the synthesized Ni(II) complex were tested for in vitro antimicrobial activity by the well diffusion method using the agar nutrient as the medium. The antibacterial and the antifungal activities of the ligands and the Ni(II) complex were evaluated by the well diffusion method against the strains, cultured on potato dextrose agar as medium. In this typical procedure a well was made on the agar medium inoculated with the microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated for 24 hours for bacteria and 72 hours for fungi at 35oC. At the end of the period, the inhibition zones formed on the medium were evaluated as millimeters (mm) diameter [16,17].

3.2. Antioxidant activity

Evaluation of antioxidant activity stock solution (1 mg/ml) was diluted to final concentrations of 10–500 µg/ml. Ethanolic DPPH solution (1 ml, 0.3 mmol) was added to sample solutions in DMSO (3 ml) at different concentrations (10–500 µg/ml). The mixture was shaken energetically and acceptable to stand at room temperature for 30 min. The absorbance was then measured at 517 nm in a UV-Vis Spectrophotometer. The lower absorbance of the reaction mixture indicates higher free radical scavenging activity. Ethanol was used as the solvent and ascorbic acid as the standard. The DPPH radical scavenging activity was designed by the following equation [18].

where Ao is the absorbance of the control reaction and A1 is the absorbance in the presence of the samples or standards.

4. Results and Discussion

4.1. Elemental analysis and metal estimation

From the elemental analytical data, the molecular formula for the Ni(II) complex was determined. It is well consonance with the hypothetical values. The analytical data are given in the Table 1. The experimental value is in good agreement with the theoretical value (given in the parentheses).

Table1. Analytical data of Ni(II) metal complex

Complex	Elements found (Calc) %				Λm ($\Omega^{-1}cm^2mol^{-1}$)
	C	H	N	M	
$[Ni(BEN)_2(TLD)_4]$	44.57 -44.88	2.81 -2.99	5.11 -5.23	10.81 -10.97	79.5

4.2. Molar conductance

Molar conductance measurements of the complex carried out using acetonitrile as the solvent at the concentration of 10-3M indicates non-electrolytic nature of the complex and the conductivity value were found to be 79.5 Ω-1cm2mol-1. Thus the prepared complex is non-electrolytic nature and there is no ion present in the outer side of the coordination sphere [19].

4.3. Magnetic moment and electronic spectra

The Ni(II) complex showed three transitions as expected , the Ni(II) complex shows three prominent bands at 617 nm (ν 1); 340 nm (ν 2); 280 nm (ν 3), which may be tentatively assigned to the transitions 3T2g(F) ← 3A2g, 3T1g(F) ← 3A2g, 3T1g(P) ← 3A2g arising from the octahedral geometry. The Ni(II) complex possesses an effective magnetic moment value of 2.95 BM which is further confirmed by an octahedral arrangement around Ni(II) metal ion [20].

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4.4. FT-IR spectra

The FT-IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the bonding mode of free ligands to the metal complex, the IR spectra of the free ligands are compared with the metal complexes. The free ligand 2,4-thiazolidinedione exhibited a strong band at 3335 cm-1 which could be assigned as ν(N-H). The peak at 2922 cm-1 assignable to the aliphatic ν(C-H) stretching frequency and ν(C=O) was revealed at 1601 cm-1 [21, 22]. The spectra showed a peak at 618 cm-1 and it could be attributed to C-S-C stretching frequency. The benzoate ion shows the frequencies 1546 cm-1 and 1605 cm-1 which may be assigned to aromatic ν(C=C) and ν(C=O) respectively. The aromatic ν(C-H) appeared at 3015 cm-1 [23,24].

The IR spectra of the complex was compared to those free ligands 2,4-thiazolidinedione and the sodium benzoate. The stretching vibrations of the ν(NH2) group were observed near 3325 cm-1 in the complex, and they were shifted lower than those of corresponding free ligand 2,4-thiazolidinedione. This shift refer to the coordination through a nitrogen atom of 2,4-thiazolidinedione. The trend is in agreement with previous examples of reported complexes. After that, the ν(C–O), which occurred at 1222cm–1 for the sodium benzoate ligand, was moved to higher frequencies after complexation, this shift confirmed the participation of carboxylic oxygen of the ligand in C–O–M bond formation [25].

5. Biological Studies

5.1. Antibacterial activity

The free ligand and its Ni(II) complex were evaluated against the bacteria staphylococcus aureus, serratia, salmonella typhi, chromo bacterium violaceum and Burkolderia) at 30 and 60 µg/ml concentration using agar-well diffusion method. The complex shows enhanced activity against salmonella typhi, chromo bacterium violaceum and moderately active against the rest of the organisms. The increased activity of the metal complexes can be explained on the basis of chelation theory [26]. It is known that chelation tends to make the ligand act as powerful and potent bactericidal agents, killing more number of bacteria than the ligand.

Table 2 Antibacterial activity of ligands and complexes

S. No	Ligand/Complex	Conc. (µg/ml)	Zone of Inhibition(mm)				
			S.aureus	*serratia*	*s. typhi*	*c. violaceum*	*Burkolderia*
1	TLD	30	7	10	9	6	5
		60	10	9	6	10	9
2	$[Ni(BEN)_2(TLD)_4]$	30	15	19	12	7	21
		60	18	25	22	26	25

05-10 Resistant; 11-16 Moderate; 16-21 Highly active; 21-26 Enhanced

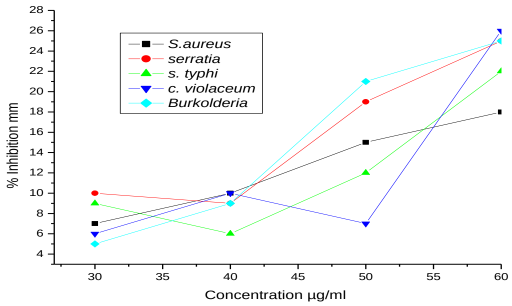

Fig.2. Antibacterial activity of ligand and Ni(II) complex

5.2. Antifungal activity

The synthesized Ni(II) complex and the free ligands were evaluated against the fungi, viz., C.albicance and Aspergillus Niger at 30 and 60 µg/ml concentration using agar-well diffusion method. The complex show enhanced activity against the tested fungus. A comparative study of zone of inhibition diameter values of the ligands and their complexes indicate that, generally, the metal complexes have a better fungicidal activity than the free ligand. This is probably due to the greater lipophilic nature of the complexes. It is evident from the data that this activity significantly increases on coordination [27].

Table 3 Antifungal activity of ligand (TLD) and Ni(II) complex.

S.No	Ligand/ Complex	Conc. µg/ml	Zone of Inhibition(mm)	
			C.albicance	*Aspergillus Niger*
1	TLD	30	12	10
		60	15	13
2	$[Ni(BEN)_2(TLD)_4]$	30	23	26
		60	27	32

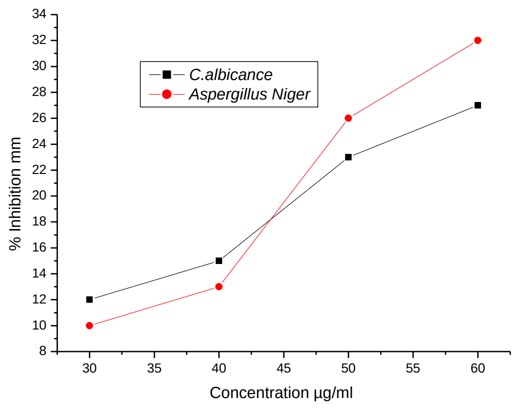

Fig.3. Antifungal activity of ligand and Ni(II) complex

5.3. Antioxidantal activity (Radical Scavenging Activity)

DPPH is a stable free radical that is often used for detection of the radical-scavenging activity in chemical analysis [28, 29]. The reduction capability of DPPH radicals was determined by the decrease in its absorbance at 517 nm which can be induced by antioxidants. [30]. A graph may be plotted with percentage scavenging effects on the y-axis and concentration (µg/mL.) on the x-axis. The metal complexes used in the study showed good activities as a radical scavenger compared to the scavenging ability of ascorbic acid, which was used as a standard. These results were in agreement with previous studies of metallic complexes [31, 32] in which the ligand has antioxidant activity and it is expected that the metal moiety will increase its activity.

Fig.3. Antioxidant activity of TLD and Ni(II) complex

Conclusion

In the present study, our efforts were to synthesize and characterize a new Ni(II) metal complex with 2,4-thiazolidinedione and benzoate ion as ligands. The new complex was synthesized using microwave irradiation. The synthesized complex was characterized by various chemical and spectral analyses. Based on the analytical, electrical conductance, spectral and magnetic moments data, octahedral geometry has been suggested for the Ni(II) complex. The prepared complex has significant antimicrobial and antioxidantal activities as compared to the free ligand (TLD).

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References

[1] BC. Ejelonu, OE. Oyeneyin, SA. Olagboye, OE Akele, Journal of Chemical and Pharmaceutical Research, 2018, 10(5): 67-73.
[2] AA El-Asmy; ME Khalifa; MM Hassanian. Indian Journal of Chemistry. 2004, 43A, 72-97.
[3] E.B. Atavo and J.P.Keheer, Free Radic. Biol. Med., 2004; 37: 36-47.
[4] Mohammed Shahnaz, Pater Kannu Bhai Ramesh Bhai, J. Drug Delivery and Therapeutics, 2013; 3 (6): 96-101.
[5] Roy, A. S.Bhanwase and T. D. Patil, Reg. J. Pharm. Biol and Chem.Sci., 2012; 3(3): 452-464.
[6] J.M Olefsky, J. Clin. Invest, 2000; 106: 467-472.
[7] BM Spiegelman, Diabetes, 1998; 47: 507-514.
[8] S.R. Pattan Reddy, V.V.K. Pawar, P.D. and A.B. Khade, Indian Drugs; 44(4), (2007), 143-147.
[9] Youssef AM, White MS, Villanueva EB, EI-Ashmavy IM, Klegeris A, Bioorg Med Chem. 2010 Mar 1;18(5):2019-28.
[10] Chavan Ameya A and Pai Nandini R. Indian Journal of Heterocyclic chemistry, 2007; 17(7): 45-48.
[11] Om Prakash, Iqbal SA and George Jacob, synthesis, physico-chemical, spectral and x-Ray diffraction studies of Zn(II) complex of Pioglitazone-a new oral antidiabetic drugs, Oriental Journal of Chemistry, 2013; 29(3): 1079-1084.
[12] Singh P, Goel RL and Singh BP, J. Indian.Chem.Soc., 1975; 52: 958.
[13] Mahindra AM, Fisher JM and Robinovitz, Nature(London), 1983; 303: 64.
[14] Ashry, E.S.H.El, Ramadan E, Kessem E, Kassem AA and Hager M, Adv. Heterocycl. Chem., 2005; 68: 1.
[15] Kappe CO and Loupy A, Microwave in Organic Synthesis (Wiley VCH, Weinheim) 2002: 405.
[16] Irobi O N, Moo – Young M and Anderson W A 1996 Int . J. Pharm. 34: 87
[17] Pelczar M.J, Chan E C S and Krieg N. R (1998) Microbiology (New York : Blackwell Science) 5th edn.,
[18] Chen. Y, Wong. M, Rosen. R. Ho, C. Thunb. (1999) J. Agric. Food Chem. 47: 2226-2228.

[19] R. Govindharaju, S. Balasubramaniyan, K. Rajasekar and T. Ramachandramoorthy, World Journal of Pharmaceutical Research, 3(7), (2014), 798-806. (ISSN 2277 –7105).

[20] R. Govindharaju, S. Balasubramaniyan, K. Rajasekar and T. Ramachandramoorthy, International Journal of Pharma Research & Review, 3(10), (2014), 8-13.l

[21] N. Raman, S. Johnson Raja, J. Joseph and J. Dhaveethu raja, J. Chil. Chem. Soc., 52(2), 1138 (2007).

[22] M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh, N. Raman and A. Kalilur Rahiman, Journal of Coordination Chemistry, 63(1), 136 (2009).

[23] Sahbaa. A. Al-Sabaawi, College of Basic Education Researchers Journal, 11(3), 765 (2011).

[24] R. Govindharaju, S. Balasubramaniyan, K. Rajasekar and T.Ramachandramoorthy, International Journal of Development Research, 2016, vol.6, no.4,, pp. 7459-7463.

[25] Neslihan Sahin, Serap Sahin Bolukbasi, Muhammad Nawaz Tahir, Cengiz Arici, Esranur Cevik, Nevin Gurbuz, Ismail Ozdemir and Brain S. Cummings, Journal of Molecular Structure, 1179, (2019), 92-99.

[26] Soares, J.R.; Dinis, T.C.P.; Cunha, A.P.; Almeida, L.M. Free Radic. Res. 1997, 26, 469-478.

[27] Duh, P.D.; Tu, Y.Y.; Yen, G.C. Lebensm. Wiss. Technol. 1999, 32, 269-277.

[28] J. R. Soares, T. C. P. Dinis, A. P. Cunha, and L. M. Almeida, Free Radical Research, vol. 26, no. 5, pp. 469–478, 1997.

[29] P. D. Duh, Y. Y. Tu, and G. C. Yen, Lebensmittel-Wissenschaft und-Technologie, vol. 32, no. 5, pp. 269–277, 1999.

[30] B. Matthaus, Journal of Agricultural and Food Chemistry, vol. 50, no. 12, pp. 3444–3452, 2002.

[31] S. B. Bukhari, S. Memon, M. Mahroof-Tahir, and M. I. Bhanger, Spectrochimica Acta Part A, vol. 71, no. 5, pp. 1901–1906, 2009.

[32] J. Gabrielska, M. Soczynska-Kordala, J. Hładyszowski, R. ´ Zyłka, J. Miskiewicz, and S. Przestalski, Journal of Agricultural and Food Chemistry, vol. 54, no. 20, pp. 7735–7746, 2006.