IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 11, Nov 2018

www.ijasrm.com

ISSN 2455-6378

Synthesis, characterization, antimicrobial and antioxidantal activities of Mn(II) complex with 2,4-Thiazolidinedione and Acetylacetanoate ion as ligands

L.Palanivelan[1], S. Balasubramaniyan[1], R. Govindharaju[2] & T. Ramachandramoorthy[3]

[1] Department of Chemistry, Govt. Arts College, Ariyalur-621 713, Tamil Nadu, India.

[2]PG & Research Department of Chemistry, Thanthai Hans Roever College (Autonomous), Perambalur-621 220, Tamil Nadu, India.

[3]PG & Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli- 620 017, Tamil Nadu, India.

Abstract

A manganese complex of the type $[Mn(ACAC)_2(TLD)_4]$, where ACAC=acetylacetanoate ion and TLD=2,4-thiazolidinedione was synthesized and characterized by elemental analysis, metal estimation, molar conductance, magnetic moment, electronic and FT-IR spectral studies. The molar conductance value indicates that the Mn(II) complex is a non-electrolyte. FT-IR spectra show that 2,4-thiazolidinedione and acetylacetanoate ion are coordinated to the metal ion in a monodentate way. The free radical scavenging activity of Mn(II) complexes have been determined by measuring their interaction with the stable free radical DPPH and the compounds have shown encouraging antioxidant activities. The in vitro antimicrobial study indicates that the complex has good activity against bacteria and fungus.

Key words: *2,4-thiazolidinedione, acetylacetanoate ion, antimicrobial and antioxidant.*

1. Introduction

During the last few decades there has been great interest in the chemistry of transition metals complexes because of their extensive applications in wide ranging areas [1]. The pharmacological activities of metal complexes depend on the nature of the metal ions and the ligands [2]. The 2,4-thiazolidinedione (TLD) is a biolologically important 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 Mn(II) complex with 2,4 - thiazolidinedione and acetylacetanoate ion ligands. The ligands and their complex are then tested for antioxidant and antimicrobial activities.

2. Experimental

2.1. Materials And Methods

Manganese nitrate, 2,4-thiazolidinedione and sodium acetylacetanoate were purchased from Alfa Aaser Company and used as such. The organic solvents used, *viz.*, DMSO, DMF, methanol and ethanol were of AnalaR grade and used as such without further purification.

IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 11, Nov 2018

www.ijasrm.com

ISSN 2455-6378

2.2. Synthesis Of Mn(II) Complex

0.9 g (7.47 mmol) of 2,4-thiazolidinedione in methanol and 1.08g (7.50 mmol) of sodium acetylacetonate in ethanol were added to the manganese nitrate 1.00g (2.50 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 blue colored complex was obtained with the yield of 90.3%.

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 Mn(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 complex were tested for *in vitro* antimicrobial activity by the well diffusion method [16], using the agar nutrient as the medium. The antibacterial and the antifungal activities of the ligands and the Mn(II) complex were evaluated by the well diffusion method against the strains, cultured on potato dextrose agar as medium. In this typical procedure [17], 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 35^{o}C. At the end of the period, the inhibition zones formed on the medium were evaluated as millimeters (mm) diameter.

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) [18]. 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:

$$\text{Scavenging effect (\%)} = \frac{A_0 - A_1}{A_0}$$

where Ao is the absorbance of the control reaction and A_1 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 Mn (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).

4.2. Molar conductance

Molar conductance measurements of the complexes carried out using acetonitrile as the solvent at the concentration of 10^{-3} M indicates non-electrolyte [19] nature of the complexes and the conductivity value were found to be 79.2 $\Omega^{-1}cm^2 mol^{-1}$. Thus the prepared complexes are non-electrolytic nature and there is no ion present in the outer side of the coordination sphere.

Table 1Elemental analysis and molar conductance

S. No.	Complex	Elements found (Calc) %				Λm
		C	H	N	M	$(\Omega^{-1}cm^2mol^{-1})$
1	$[Mn(ACAC)_2(TLD)_4]$	36.98 - 37.77	6.04 - 6.16	5.51 - 5.64	7.85 - 7.94	79.2

4.3. Mn(II) complex

The electronic spectrum of manganese (II) complex that exhibits three absorbtion bands at 605 nm, 330 nm, 262 nm indicates the three electronic excitations $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4E_g$ and CT charge transfer-spectra respectively. These three lowest energy transitions indicate the distorted octahedral geometry of the complex. This geometry is further confirmed by the magnetic moment of 4.90BM [20].

4.4. FT-IR spectra

The FT-IR spectra of the free ligands and their metal complexes were recorded in the region of 4000-400 cm^{-1}. The free ligand 2,4-thiazolidinedione exhibited a strong band at 3369

ISSN 2455-6378

cm^{-1} which could be assigned as ν(N-H). The peak at 2945 cm^{-1} assignable to the aliphatic ν(C-H) stretching frequency and ν(C=O) was revealed at 1623 cm^{-1} [21, 22]. The spectra showed a peak at 628 cm^{-1} and it could be attributed to C-S-C stretching frequency. The acetylacetanoate ion shows the frequencies 1567 cm^{-1} and 1620 cm^{-1} which may be assigned to 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 complexes were compared to those free ligands 2,4-thiazolidinedione and the sodium acetylacetanoate. The stretching vibrations of the ν(NH_2) group were observed near 3336 cm^{-1} in all the complexes, and they were lower than those of corresponding free ligand 2,4-thiazolidinedione.This indicates that the ligand 2,4-thiazolidinedione coordinate to the metals via nitrogen atom of amino group. The trend is in agreement with previous examples of reported complexes. After that, the ν(C–O), which occurred at 1211cm^{-1} for the sodium acetylacetanoate ligand, was moved to higher frequencies, near 1221-1285 cm^{-1} after complexation, this shift confirmed the participation of carboxylic oxygen of the ligand in C–O–M bond formation [25].

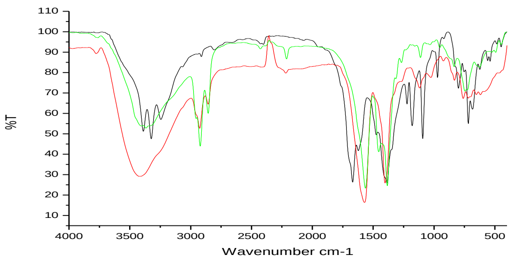

Fig.32 FT-IR spectra of TLD, NaACAC and $[Mn(ACAC)_2(TLD)_4]$

5. Biological Studies

5.1. Antibacterial activity

The free ligand and its Mn(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 complexes shows enhanced activity against *staphylococcus aureus, serratia, salmonella typhi* 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 [33]. 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/ Complexes	Con. 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	$[Mn(ACAC)_2(TLD)_4]$	30	12	17	10	18	9
		60	15	19	12	7	21

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

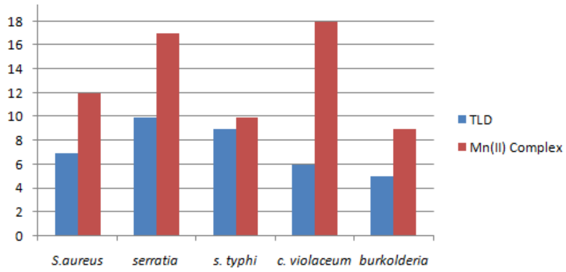

Fig.2. Antibacterial activity of ligand and complex

5.2. Antifungal Activity

The synthesized Mn(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 [34].

Table 3 Antifungal activity of ligand(TLD) and Mn(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	$[Mn(ACAC)_2(TLD)_4]$	30	18	15
		60	23	26

IJASRM
International Journal of Advanced Scientific Research and Management, Volume 3 Issue 11, Nov 2018
www.ijasrm.com
ISSN 2455-6378

5.3. Antioxidantal activity (Radical Scavenging Activity)

The 2,2″-diphenyl-1-picrylhydrazyl (DPPH) radical assay provides an easy and rapid way to evaluate the antiradical activities of antioxidants. Determination of the reaction kinetic types DPPHH is a product of the reaction between DPPH• and an antioxidant.

(AH): DPPH$^{\bullet}$ + AH → DPPH-H + A$^{\bullet}$

The reversibility of the reaction is evaluated by adding DPPHH at the end of the reaction. If there is an increase in the percentage of remaining DPPH$^{\bullet}$ at the plateau, the reaction is reversible, otherwise it is a complete reaction. DPPH was used as stable free radical electron accepts or hydrogen radical to become a stable diamagnetic molecule [26]. DPPH is a stable free radical containing an odd electron in its structure and usually used for detection of the radical scavenging activity in chemical analysis [27]. The reduction capability of DPPH radicals was determined by decrease in its absorbance at 517 nm induced by antioxidants [28]. The graph was plotted with percentage scavenging effects on the y-axis and concentration (µg/ml.) on the x-axis. The scavenging ability of the free ligands and their Mn(II) complex were compared with ascorbic acid as a standard. The Mn(II) complex showed enhance activities as a radical scavenger compared with ascorbic acid, these results were in good agreement with previous metal complexes studies where the ligand has the antioxidant activity and it is expected that the metal moiety will increase its activity [29-32].

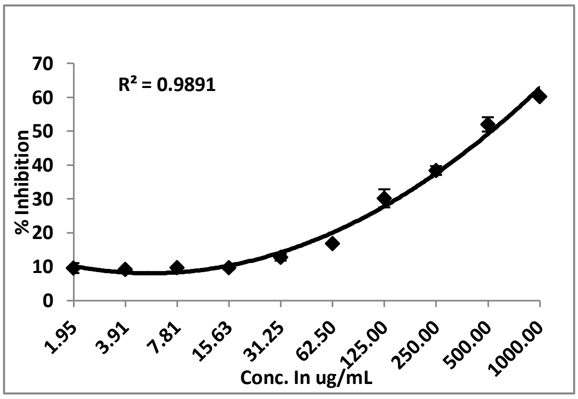

Fig.3. Antioxidant activity of Mn (II) complex

6. Conclusion

In the present study, our efforts were to synthesize and characterize a new Mn(II) metal complex with 2,4-thiazolidinedione and acetylacetanoate 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 Mn (II) complex. The prepared complex has significant antimicrobial and antioxidantal activities as compared to the free ligand(TLD).

Acknowledgement

The authors wish to thank the Principal for providing the infrastructural facilities in the Department of Chemistry, Government Arts College, Ariyalur, Tamil Nadu, India. They also thank to the Head and Staff members of STIC, Cochin University, SAIF,IIT, Mumbai and SAIF,IIT, Chennai for providing instrumental data.

References

[1] L.J.K. Boerner and J.M. Zaleski, Curr.Opin. Chem. Biol. 9: 135-144 (2005).
[2] Colak, U. Terzi, M.Col, S. Engul alpay karaoglu, S. Karabocek, A. Kucukdumlu and F. Ahmet Ayaz, Eur.J. Med. Chem. 45: 5169-5175 (2010).
[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, L. Palanivelan and T. Ramachandramoorthy, IOSR Journal of Applied Chemistry, (IOSR-JAC), 9(5), (2016), 37-41. (e-ISSN: 2278-5736)
[20] M. N. Patel and V. J. Patel, Inorg. Met-Org. Chem., 19, (1989), 137-155.
[21] R. Govindharaju,S. Balasubramaniyan, K. Rajasekar and T.Ramachandramoorthy, International Journal of Development Research, 2016, vol.6, no.4,, pp. 7459-7463.
[22] N. Raman, S. Johnson Raja, J. Joseph and J. Dhaveethu raja, J. Chil. Chem. Soc., 52(2), 1138 (2007).
[23] M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh, N. Raman and A. Kalilur Rahiman, Journal of Coordination Chemistry, 63(1), 136 (2009).
[24] Sahbaa. A. Al-Sabaawi, College of Basic Education Researchers Journal, 11(3), 765 (2011).
[25] Ram N. Patel, Vishnu P. Sondhiya, Krishan K.Shukla and Dinesh K.Patel, Polyhedron, 50 (2013) 139.
[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] Matthaus, B.J. Agric. Food Chem. 2002, 50, 3444 ‐ 3452.
[29] Bukhari, S.B.; Memon, S.; Mahroof-Tahir, M.; Bhanger, M.I. Spectrochim. Acta A Mol. Biomol. Spectrosc.2009, 71, 1901-1906.
[30] Gabrielska, J.; Soczynska-Kordala, M.; Hladyszowski, J.; Zylka, R.; Miskiewicz, J.;
[31] Przestalski, S. J. Agric. Food Chem. 2006, 54, 7735-7746.
[32] Bukhari, S.B.; Memon, S.M.; Tahir, M.M.; Bhanger, I.J. Mol. Struct. 2008, 892, 39-46.
[33] Rohaya, A.; Abdul Manaf, A.; Daud, A.; Israf, T.; Nor, H.; Khozirah, S.; Nordin, H. Life Sci. 2005, 76, 1953-1964.
[34] Bertoncello, G. D. Fallon and E. R. T. Tiekink, Inorg. Chem., 30, (1991), 3562.