Research Journal of Chemical Sciences _____ E-ISSN 2231-606X
Vol. **6(11),** 44-47, November **(2016)** *Res. J. Chem. Sci.*

Short Communication

Efficient Ultrasound Synthesis, Spectral studies of 1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propane-1, 3-dione with metal complexes as antibacterial and antifungal agents

Dayanand M. Suryawanshi[1], Vijayanand D. Ingale[2], Anjali S. Rajbhoj[2] and Suresh T. Gaikwad[2*]
[1]Department of Chemistry, Rayat Shikshan Sanstha's Annasaheb Awate College, Manchar (M.S.), India 410 503
[2]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.) India 431 004
gaikwadsuresh12@gmail.com

Available online at: www.isca.in, www.isca.me
Received 22nd August 2016, revised 15th November 2016, accepted 17th November 2016

Abstract

*The newly synthesized 1-(2-hydroxy phenyl)-3-(4-nitrophenyl) propane-1, 3-dione with their transition metal (II) complexes **5(a-e)** under ultrasound irradiation methods at low temperature were characterized by elemental analysis, FTIR, ^{1}H-NMR spectrum, Mass, and Electronic spectroscopy. The ratio of the metal (II) complexes was found to be 1:2 (metal: ligand). The analytical data suggested that octahedral geometry for the all complexes. The synthesized ligand and their metal complexes **5(a-e)** were screened for antimicrobial activity against S. aureus, B. Subtilis and A. Niger and F. Oxysporum using streptomycin as a references drugs.*

Keywords: 1, 3-diones, Metal complexes, Ultrasound irradiations, Antibacterial and Antifungal screening.

Introduction

The metal (II) complexes of 1, 3-dione derivatives have broad spectrum such as organic electroluminescent technology, luminescent and sensors optical materials[1-3]. They have also used in healthcare, both as active pharmaceutical ingredients (or substrates for the manufacture of medicines) and cosmetic additives which reduce the detrimental effects of UV radiations on the skin[4].

The synthesized ligands and their transition metal (II) complexes show antimicrobial, antimalarial and antitumor[5-6], antioxidants[7], insecticidal activity[8] and bioinorganic applications[9-11].These compounds have interest in nucleic acid chemistry as well as their use in biomedicine[12-15].

The 1, 3-diones and their transition metal (II) complexes have pharmacological activities as well as good agreement of result of antibacterial[16] and antifungal activities[17]. This paper reports that synthesis of ligands with their transition metal (II) complexes, spectral analysis and antimicrobial screening of the compounds. The antimicrobial studies were shown in the Table-2.

Materials and Methods

The substituted ortho hydroxy acetophenone and 4-nitrobenzoic acid were SD fine products. The UV-Vis spectrum of the ligands and their complexes were recorded by Shimadzu UV-1800 Spectrophotometer. IR spectrums were recorded on Shimadzu FT-IR-4100 spectrometer using KBr pallets. ^{1}H-NMR spectrums of the ligand was recorded using a Bruker DRX-500 MHz NMR spectrometer. Mass spectrum was recorded on a Macro Mass spectrometer.

***Synthesis of 2-acetylphenyl 4-Nitro benzoate* (3):** A reaction mixture of ortho hydroxy acetophenone (1.70 g, 0.01 mol) and 4-nitro benzoic acid (1.66 g, 0.01 mol), in a dry pyridine. A drop wise addition of $POCl_3$ for maintaining temperature 0^0C. It was irradiated for about 2-3h under ultrasound irradiations at low temperature. The reaction mixture was poured into 1M HCl containing 50 gm crushed ice with vigorous stirring. The solid (ester) was obtained. It was further filtered, washed with ice-cold methanol. It was crystallized with distilled ethyl alcohol. (Yield: 85% m. p.: 78 ^{0}C).

***Synthesis of 1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propane-1, 3-dione* [HL]**: A Compound (**3**) was dissolved in 15 ml dry pyridine. To the addition of powdered KOH was irradiated for about 1-2 h. It was poured over crushed ice the resulting solid (**4**) was crystallized from distilled ethyl alcohol. (Yield: 82%); m.p.132 ^{0}C.) ^{1}H-NMR, 14.80 δ (s, 1H, enolic -OH), 11.87 δ (s, 1H, Phenolic –OH) 7.49 δ (s, 1H, =C-H ethylene), 6.54-7.98 δ (m, 8H, Ar-H); IR (KBr) ν_{max}/cm^{-1}; 1735 (ν (C=O) ketonic), 1199 (ν (C-O) enolic), 3099 (ν (-OH) intramolecular H-bonding in Phenolic). UV/Vis. (DMSO) nm: 399, 340. MS *m/e*: 285.06

***Synthesis of complexes* 5(a-e)**: The transition metal (II) complexes were obtained by the hot solution of the metal (II) nitrate (10 mmol) in ethanol (25ml) were mixed with the hot

solution of the 1-(2-hydroxy phenyl)-3-(4-nitrophenyl) propane-1, 3-dione (10 mmol) in the same solvent. It was irradiated for about 1h under ultrasound irradiation at high temperature. The complexes were dried in vacuum. (Yield: 82-87%) IR (KBr) ν_{max}/cm^{-1}; 1665-1680 (ν(C=O) ketonic), 1203-1209 (ν(C-O) enolic), 3072 (ν (-OH) intramolecular H-bonding in Phenolic), 3435-3462 (ν (-OH) in H_2O molecules) 450-465 (ν (M-O bond in complex); UV/Vis. (DMSO) nm: 271 ($\pi \rightarrow \pi^*$), 398 (LMCT) , 672-674 (d-d transition).

Results and Discussion

The synthesized ligands are confirmed by ^{1}H-NMR**,** Mass, IR and electronic spectra. Comparative studies of conventional and nonconventional results of the ligand and their metal complexes are given in Table-1. The physico-chemical data suggested that octahedral geometry for the all complexes[18-21].

The characteristics peak at 3470 cm^{-1} in IR spectrum due to aromatic –OH group. The band appear at 1735cm^{-1} due to (C=O) group, it exhibited at lower shift in metal complexes indicate that the keto-enol tautomer in ligands. The new bands appear at 450-465 cm^{-1} due to metal-oxygen.

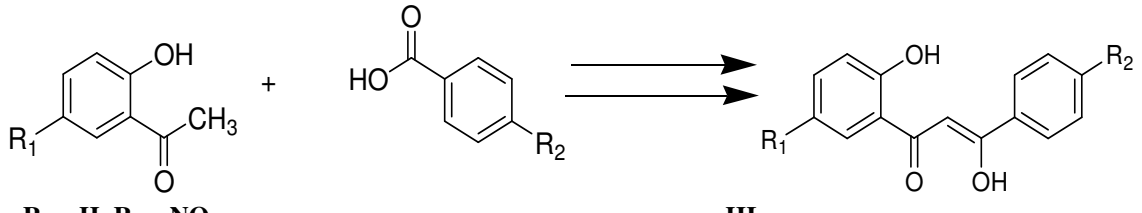
In the ^{1}H-NMR ($CDCl_3$-d_6) it gives characteristics peaks at δ 14.80 for enolic proton and at δ 11.87 for phenolic proton. It confirms the formation of 1, 3 –diketones. The antimicrobial activities of ligands and their metal complexes observed that metal (II) complexes showed more potent' than free ligands.

Antimicrobial Screening: In vitro antibacterial activity of the synthesized compounds were tested against *S. Aureus, B. Subtilis* and antifungal activity against *A. Niger* and F. *Oxysporum* by disc diffusion techniques using dimethyl sulphoxide as a solvent. The obtained results were camparable with standard drug streptomycin[22-26]. The results are good agreements with standard drugs are given in Table-2.

Amongst all the Samples 5 (a-d) only samples 5(c) and 5(d) were found to be highest antibacterial activities against *S. aureus* and *B. Subtilis* at 250 and 500ppm while sample 5(a) and 5(d) have showed highest antifungal activities against *A. Niger* and *F. Oxysporum* at same concentration. From the Table-2 it is clear that, the results of antimicrobial activities of metal (II) complexes is more potent than free ligands.

Table-1
Comparative studies of ligand and their metal (II) complexes

Compound	Mol.Wt.	M.P./decomp. Temp (^{0}C)	Conventional		Ultrasound Irradiation	
			Time (min)	Yield (%)	Time (min)	Yield (%)
$C_{15}H_{11}NO_5$	285.25	132	340	68	120	82
$C_{30}H_{24}MnN_2O_{12}$	659.46	272	280	72	90	86
$C_{30}H_{24}FeN_2O_{12}$	660.36	324	280	68	90	84
$C_{30}H_{24}CoN_2O_{12}$	663.45	268	280	70	90	85
$C_{30}H_{24}NiN_2O_{12}$	663.21	213	280	73	90	83
$C_{30}H_{24}CuN_2O_{12}$	668.06	239	280	74	90	87



R_1 = H, R_2 = NO_2 **HL**

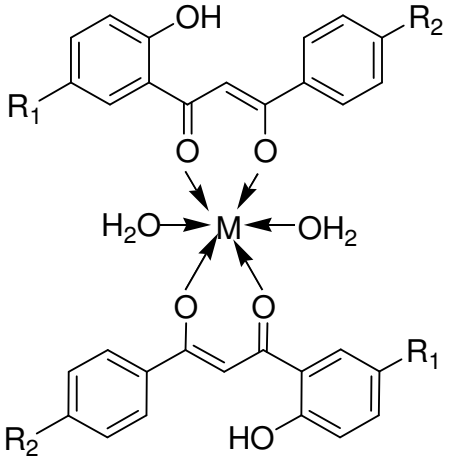
Scheme-I
Synthesis of Ligands

Table-2
Antimicrobial screening of the synthesized compounds

Ligand / Metal Complexes	Antibacterial activity				Antifungal activity			
	S. aureus		*B. Substilis*		*A. Niger*		*F. Oxysporum*	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
[HL]	17	19	19	24	18	30	18	25
5(a)	18	22	16	20	19	20	20	21
5(b)	17	22	16	17	16	18	14	18
5(c)	16	20	13	19	19	20	15	17
5(d)	12	17	12	19	20	22	16	20
Streptomycin	**15**		**17**		**19**		**21**	

Conclusion

The newly synthesized 1-(2-hydroxy phenyl)-3-(4-nitrophenyl) propane-1, 3-dione (HL) and its metal complexes 5(a-e) were characterized by spectral analysis. An efficient ultrasound irradiation assisted organic synthesis are safe eco-friendly synthetic strategy for improve yields. All these metal complexes were more potent antibacterial and antifungal activities than the parent ligands. In conclusion, these compounds have a drug likeness.



M= Mn(II), Fe(III), Co(II), Ni(II), Cu(II)
Figure-1
Proposed Structure of Metal Complexes

Acknowledgment

The authors are thankful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad and UGC-SAP-DRS Scheme-1, for providing necessary laboratory facilities, Department of Chemistry, Annasaheb Awate College, Manchar.

References

1. Bray D.J., Clegg J.K., Lindoy L.F. and Schilter D. (2007). Synthetic, structural, electrochemical and solvent extraction studies of neutral trinuclear Co(II), Ni(II), Cu(II) and Zn(II) metallocycles and tetrahedral tetranuclear Fe(III) species incorporating 1,4-aryl-linked bis-b-diketonato ligands. *Adv. Inorg. Chem.,* (59), 1-37.

2. Aromi G., Gamez P. and Reedik J. (2008). Poly beta-diketones: Prime ligands to generate supramolecular metalloclusters. *Coord. Chem. Rev.,* (252), 964–989

3. Alessandro Vigato P., Valentina Peruzzo and Sergio Tamburini (2009). The evolution of β-diketone ligands and related complexes. *Coord. Chem. Rev.,* (253), 1099–1201,

4. Aho P., Backstrom R., Honkanen E., Linden I., Nissien E. and Pohto P. (1994). nr 163044 BI. PL Patent.

5. Acton N., Brossi A., Newton D.L. and Sporn M.B. (1980). Potential prophylactic antitumor activity of retinylidene 1,3-diketones. *J. Med. Chem.,* (23), 805-809.

6. Dalal A., Kamboj R.C., Kumar D., Sharma M.K. and Selvarajan N. (2015). Crystal structure of (Z)-3-[5-chloro-2-(prop-2-ynyloxy)phenyl]-3-hy-droxy-1-[4-(trifluoromet hyl)phenyl]prop-2-en-1-one. *Acta Cryst.,* E71, 556-557.

7. Nishiyama T., Shiotsu S. and Tsujita H. (2002). Antioxidative activity and active site of 1,3-indandiones with the β-diketone moiety. *Polym. Degrade. Stab*, (76), 435-439.

8. Crouse G.D., McGowan M.J. and Boisvenue R.J. (1989). Polyfluoro 1,3-diketones as systemic insecticides. *J. Med. Chem.,* (32), 2148-2151

9. Hemmila I.A. (1991). Applications of Fluorescence in Immunoassay. Wiley, New York, ISBN: 0-85186-225-x

10. Sabbatini N., Guardigli M. and Lehn J.M. (1993). The chemistry of Metal-Organic Framework. *Coord. Chem.*, (123), 201–228

11. Zhimin Chen, Wu. Yiqun, Fuxin. Huang, Gu. Donghong and Fuxi. Gan, (2007). Spectroscopic and thermal properties of short wavelength metal (II) complexes containing alpha-isoxazolylazo-beta-diketones as coligands. *Spectrochim. Acta Part A.,* (66), 1024–102.

12. Karvembu R. and Natarajan K. (2002). Synthesis and spectral studies of binuclear ruthenium (II) carbonyl complexes containing bis (β-diketone) and their applications. *Polyhedron*., (21), 219–223

13. Huaqiang Zeng, Jianming Xie and Schultz P.G. (2006). Genetic introduction of a diketone-containing amino acid into proteins *Bioinorg. Med. Chem. Lett.*, (16), 5356-5359.

14. Ameerunisha Begum M.S., Sounik Saha, Akhtar Hussiain and Chakravarty A.R. (2009). Synthesis, Crystal Structure of DNA cleavage of Copper (II) Complexes. *Indian J.Chem,* (48A), 9-14,

15. Raman N., Mitu L., Sakthivel A. and Pandi M.S.S. (2009). Studies on DNA cleavage and antimicrobial screening of transition metal complexes of 4-aminoantipyrine derivatives of N_2O_2 type. *J. Iran. Chem. Soc.,* (6), 738–748.

16. Bennett I., Broom N.J.P., Cassels R., Elder J.S., Masson N.D. and O'Hanlon P.J. (1999). Synthesis and antibacterial properties of beta-diketone acrylate bioisosteres of pseudomonic acid. *Med. Chem. Lett.,* (9), 1847-1852

17. Kumari Neetu, Yadav Pradeep and Joshi Yogesh C. (1978). Synthesis of Some Novel β-Diketones and β-Ketoesters of 4-Methyl Sulphonyl Benzoyl Methylene Bromide. *Chem. Sci Trans.,* 2(1), 81-84.

18. Korde N.S., Gaikwad S.T., Khade B.C. and Rajbhoj A.S. (2013). Efficient Ultrasound Synthesis, Characterizations and Antimicrobial Screening of Novel Cyclic *β*-Diketones. *Chem. Sci. Trans.,* (2),

19. Korde N.S., Gaikwad S.T., Korde S.S. and Rajbhoj A.S. (2013). Ultrasound synthesis, characterization and thermal study of some ransition metal complexes of β-diketone ligand. *J. of Rec. Tech. and Engin*. (2), 4.

20. Kumar U. and Chandra S. (2011). Mn(II), Co(II), Ni(II), & Cu(II) Complexes of Nitrogen and Sulphur Donar ligands. *J. Saudi Chem. Soc.* (15), 187–193

21. Munde A.S., Jagdale A.N., Jadhav S.M. and Chondhekar T.K. (1979). Synthesis, characterization and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand. *Journal of Serbian Chemical Society,* 75(3), 349-359.

22. Sing D.P., Kumar R., Malik V. and Tagi P. (2007). Template synthesis and characterization of biologically active transition metal complexes comprising 14-membered tetraazamacrocyclic ligand. *Journal of Serbian Chemical Society,* 75(2), 217-228.

23. Chandra S., Tyagi M. and Agrawal S. (2010). Synthesis and characterization of a tetraaza macrocyclic ligand and its cobalt (II), nickel (II) and copper(II) complexe. *J. Serb. Chem. Soc.,* 75(7) 935–941.

24. Chandra S., Tyagi M. and Agarwal S. (2010). Antibacterial and antifungal activity of Schiff base ligands and their metal complexes. *Serb. Chem. Soc.*, 75(7), 935–941.

25. Hunter T.M., Paisley S.J. and Park H.S. (2004). Investigations of internal mannich Reactions. *J. Inorg. Biochem*, (98), 713

26. Athira C.J., Sindhu Y., Sujamo M.S. et. al. (2006). Synthesis and spectroscopic characterization of some Lanthanide (III) nitrate complexes of ethyl 2-[2-(1-acetyl-2--isopropyl) Azo]-4,5-dimethyl-3-thiophenecarboxyat. *Russ. J. Coord. Chem.,* 76(2), 249-261.