ISSN:1991-8178

Australian Journal of Basic and Applied Sciences

Journal home page: www.ajbasweb.com

Microwave Assisted Synthesis of Biologically Active Cd(II) and Hg(II) Metal Complexes With Schiff's Base and Thiocyanate Ion

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ARTICLE INFO

Article history:
Received 12 March 2015
Accepted 28 April 2015
Available online 5 May 2015

Keywords:
SBPS, Thiocyanate, Cd(II) & Hg(II) complexes, Antibacterial and Antifungal

ABSTRACT

Transition metals of Cd(II) and Hg(II) complexes were prepared with Schiff's base of phenylacetylurea with salicylaldehyde (SBPS) and thiocyanate ion as ligands under microwave irradiation. Synthesised complexes were characterized from elemental analysis, metal estimation, molar conductance, UV-visible, IR, Far-IR and NMR spectral studies. The ligand has been synthesized by the condensation of phenylacetylurea and salicylaldehyde. In elemental analysis and metal estimation the complexes show 1:1 ratio of composition of each ligands $[ML_2X_2]$ where M=Cd(II) and Hg(II), L=SBPS and X=SCN^-. The molar conductance values indicate the non-electrolytic (1:0 type) of the complexes. Pseudotetrahedral geometry, entry of ligands from UV and IR spectra, metal linked atom from Far-IR spectral data were deduced. Proton and carbon types were also identified from NMR spectral data. Antibacterial and antifungal activities of the Schiff's base and its metal complexes were carried out by Kirby Bauer disc diffusion method. The results show that complexes have more activity than the Schiff's base.

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To Cite This Article: P. Durairaj, T. Maruthavanan, S. Manjunathan and K. Rajasekar., Microwave Assisted Synthesis of Biologically Active Cd(II) and Hg(II) Metal Complexes With Schiff's Base and Thiocyanate Ion ***Aust. J. Basic & Appl. Sci.,*** *9(11): 214-218, 2015*

INTRODUCTION

In recent times there is an enhanced interest in the synthesis of transition metal containing Schiff's base. Schiff's base has several applications in biological, clinical and analytical fields.[1] due to their enhanced biological and pharmaceutical activities and the Schiff's base have attracted many workers.[2] Schiff's base ligand complexes are very important in many catalytic reactions.[3] It is also used in the di-oxygen uptake and oxidative catalyst.[4-5]Microwave-assisted reactions are eco-friendly technique and it is a branch of Green Chemistry. This technique is certainly going to be the technology of tomorrow. The advantages of microwave reactions over conventional techniques are fast, clean, economic, pollution free, shorter time high yield.[6-7] In the present paper, the Schiff's base is derived from phenylacetylurea and salicylaldehyde by condensation which is used in primary ligand for the preparation of Cd(II) and Hg(II) complexes. The prepared complexes were characterized by the physico-chemical and spectral studies.

MATERIALS AND METHODS

Experimental:

1) Materials:

Phenylacetylurea, Salicylaldehyde (Merck), Sodium thiocyanate, Cadmium nitrate, Mercury chloride, DMSO, DMF, methanol, ethanol were of AnalaR grade, and used as such without further purification.

2) Methods:

a) Preparation of Schiff's base ligand:

The ligand Schiff's base is prepared by the condensation of phenylacetylurea with salicylaldehyde refluxed with alcohol in the presence of NaOH.

b) i. Preparation of Cd(II) complex:

Cadmium nitrate 1.00g (2.92 mmol) is dissolved in methanol, Schiff's base (SBPS) 2.41 g (8.77 mmol) dissolved in methanol was added in drops with constant stirring; The mixture was irradiated in a microwave oven for about 10 seconds. Then sodium thiocyanate 1.10 g (8.77 mmol) dissolved in ethanol was added to the above solution and the

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whole mixture was irradiated in a microwave oven for 10 seconds. The precipitated complex was filtered, washed with ethanol and dried.

ii. Preparation of Hg(II) complex:

Mercury chloride 1.00g (2.49 mmol) is dissolved in methanol, Schiff's base (SBPS) 2.06 g (7.49 mmol)is dissolved in methanol were added in drops with constant stirring; The mixture was irradiated in a microwave oven for about 10 seconds. Then sodium thiocyanate 0.95 g (7.49 mmol) dissolved in ethanol was added to the above solution and the whole mixture was irradiated in a microwave oven for 10 seconds. The precipitated complex was filtered, washed with ethanol and dried.

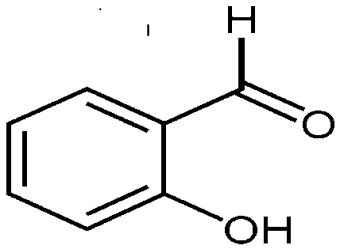


Fig. 1: Structure of Salicylaldehyde.

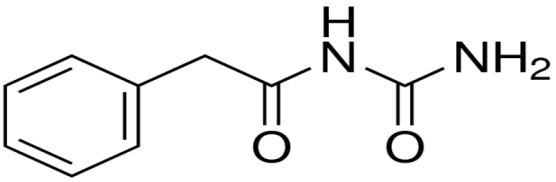
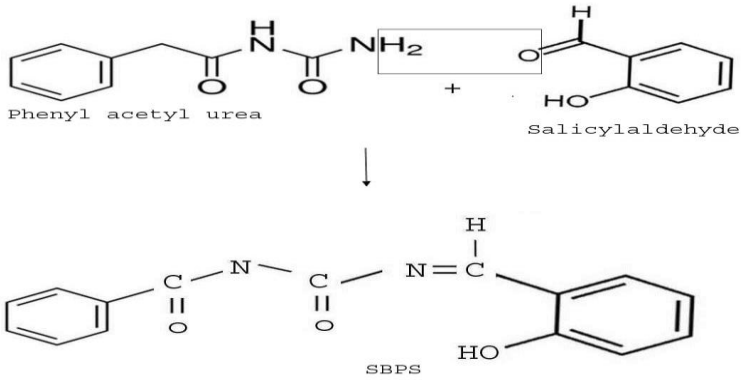


Fig. 2: Structure of Phenyl acetyl urea.



c) Instrumental techniques:

The elemental analysis of the complexes was carried out by using (Thermo Finnigan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The molar conductance measurements were conducted using 10^{-3} M solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge 304 at 30°C. The UV spectra of Cd(II) and Hg(II) complexes were recorded on a Varian make, Cary 5000 model, UV-visible Spectrophotometer. The IR spectra of the ligand and its complexes were recorded by using Perkin Elmer, Spectrum RX-I, FT-IR spectrometer in 4000-400 cm^{-1} ranges with KBr pellet technique. The Far-IR Spectrum of the complexes was recorded by Bruker 3000, FT- IR Spectrometer. The ^{1}H NMR and ^{13}C NMR spectra of the ligand and its complexes were recorded by 500 MHz FT-NMR Spectrometer in DMSO-d6 using TMS as the internal standard. The antibacterial and antifungal activities of the ligand and its complexes were recorded by the Kirby Bauer disc diffusion method using Amikacin and Ketoconazole as standard and DMSO as solvent.

RESULTS AND DISCUSSION

i) Elemental Analysis

The elemental analysis data of the complexes are consistent with the calculated results from the empirical formulae of each compound. The values found are in good agreement with the theoretical ones.

ii) Metal Estimation:

Metal ions of the prepared complexes were estimated volumetrically and gravimetrically by using the standard procedure. The percentage of metal ion in each complex is in good agreement with its formula derived from the elemental analysis.

iii) Molar Conductance:

The metal complexes were dissolved in CH_3CN and the molar conductivities of their 10^{-3} M solutions were measured at 30°C. The low molar conductance (308.48 and 271.49 $ohm^{-1}cm^2mol^{-1}$) shows the non electrolytic nature (1:0 type) of the complexes.[8] From the elemental analysis, metal estimation and molar conductance values are predicted. They show that the complexes may have the stoichiometry of $[ML_2X_2]$ respectively where M = Cd(II) and Hg(II), L=SBPS & X=SCN^-.

iv) UV-Spectra:

The complexes of $[Cd(SBPS)_2(SCN)_2]$ and $[Hg(SBPS)_2(SCN)_2]$ gave only charge transfer transitions (CT band) at 255 nm (39,215 cm^{-1}) and at 260 nm (38, 461 cm^{-1}) respectively. The most probable geometry of Cd(II) and Hg(II) complexes are pseudo tetrahedral.[9]

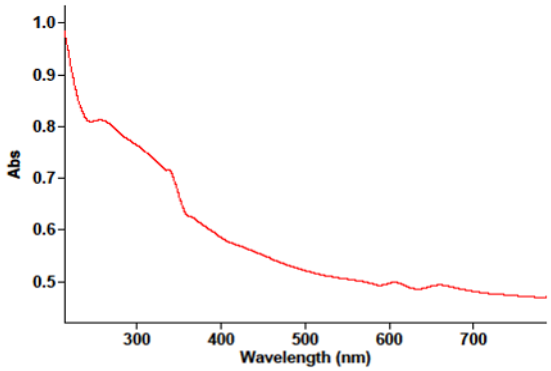


Fig. 3: UV-spectrum of Cd(II) complex.

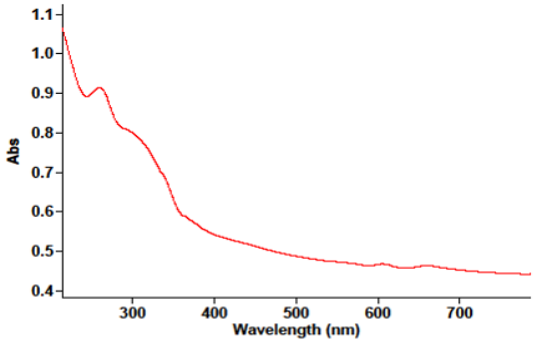


Fig. 4: UV-spectrum of Cd(II) complex.

v) IR and Far-IR spectra:

IR spectrum of the pure ligand shows the characteristic frequencies as follows: at 3388cm^{-1} it indicates the ν(N-H) stretching frequency of primary amine and at 1668 cm^{-1} indicates the symmetric stretching frequency and at 1622 cm^{-1} the asymmetric stretching frequency of ν(N-H) in secondary amine. The ν(C=O) stretching frequency of the ligand is observed at 1475cm^{-1}. In Cd(II) and Hg(II) complexes, except ν(N-H) of secondary amine asymmetric stretching frequency all the other frequencies are shifted to slightly higher or lower values but in secondary amine the symmetry stretching frequency at (1668 cm^{-1}) is slightly shifted to 1668 cm^{-1}. But the asymmetric stretching frequency (1622cm^{-1}) is shifted to lower values of 1612 cm^{-1} in Cd(II) and at 1702 cm^{-1} and 1673 cm^{-1} in Hg(II) complex which is confirms the entry of ligand into the coordination sphere. Most of the thiocyanate complexes are N-bonded coordination modes. The IR spectra of the complexes prepared are also compared with the spectra reported for the thiocyanato complexes. The C-N stretching frequency of N-bonded complexes is nearly 2050 cm^{-1}, lower than that of S-bonded (nearly 2100 cm^{-1}). It is moved by 40-20 cm^{-1} to higher frequency range in all the complexes. The C-S stretching for N-bonded complexes at 800-751 cm^{-1} is present in all the complexes.[10-11]

Far-IR Spectra[12]:

The Far-IR spectrum gives the information about the metal linked atom frequency. In Cd(II) and Hg(II) complexes, the ν(M-N) (secondary amine) coordination at 443 cm^{-1} and 434 cm^{-1} respectively indicate the coordination through the nitrogen atom (secondary amine) of Schiff's base. The weak band at 487 cm^{-1} and 471 cm^{-1} were assigned δ(M-NCS) and this indicates the coordination of metal ion through nitrogen atom of SCN^- ion.

^{1}H-NMR spectra:

Proton NMR spectrum of the ligand shows the chemical shift values as follows: at 10.38 ppm indicates the N-H group and at 7.23 - 7.68 ppm (multiplet) indicates the aromatic phenyl group. In Cd(II) and Hg(II) complexes the N-H chemical shift value moves towards downfield at 10.36-10.37 ppm which is confirming the entry of the ligand into the coordination sphere.

^{13}C-NMR spectra:

In ^{13}C-NMR spectrum the chemical shift value at 173.19 ppm(C=O), 154.34 ppm (C-NH), 127.26-127.29 ppm (p-carbon), 128.81-129.72 ppm (o-carbon), 135.26 (m-carbon). The chemical shift values at 42.96 ppm indicating the SCN^- carbon atom. In Cd(II) and Hg(II) complexes the N-H chemical shift values are moved towards downfield at 154.33 ppm.

Antimicrobial activities[13-14]:

The antibacterial activities and antifungal activities of Schiff's base ligands and its metal complexes were tested against *E.coli, Klebsiella Pneumoniae, P. Aeruginosa, S. aureus and Bacillus cereus.* Ketoconazole and Amikacin were used as a standard for antifungal and antibacterial activities of the tested microorganisms.

The results indicate that the complexes showed good biological activity against the tested microorganisms. The inhibition zone of the metal complexes which is higher than pure ligand can be explained on the basis of overtone concept and chelation theory.

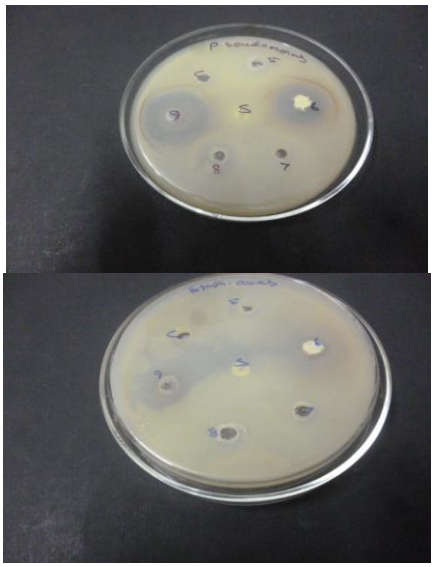


Fig. 5: Zone of inhibition of Cd(II) and Hg(II) complexes.

Conclusion:

The Schiff's base of Phenylacetylurea and salicylaldehyde complexes have been synthesised and characterized by using elemental analysis, metal estimation, molar conductance, UV, IR and Far-IR spectra and NMR spectral studies. The results are confirmed by the pseudo tetrahedral geometry and the non-electrolytic nature of the complexes with 1:1 stoichiometry ratio. Antibacterial and antifungal activities are also confirmed by the biological activities more than those for the pure ligand.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, SAIF, IIT and the Director, STIC, Cochin for providing the spectral data collection. The authors also thank the Managements and the Principals of Sona College of Technology, Salem and Dr. Navalar Nedunchezhiyan College of Engineering, Tholudur for permitting them to carry out this work.

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