Available online at www.scientiaresearchlibrary.com

Scientia Research Library

ISSN 2348-0408
USA CODEN: JACGON

Journal of Applied Chemistry, 2016, 4 (2):9-16

(*http://www.scientiaresearchlibrary.com/arhcive.php*)

SPECTRAL, REDOX AND BIOLOGICAL CHARACTERIZATION OF NEWLY SYNTHESIZED Co(II) AND Ni(II) COMPLEXES OF AMPYRONE AND OXALATE ION

K. Rajasekar[1], K. Kanagaraj[2], S. Naveen Kumar[2], R. Rajiv Ganthi[2] ,R. Rajkumar[2]

1. Department of Chemistry, Government Arts College, Ariyalur-621 713, Tamil Nadu, India
2. Meenaakshi Ramasamy Arts & Science College, MR-Kalvi Nagar Thathanur-621 804, Tamil Nadu, India

ABSTRACT

Transition metal ions are easily form complexes due to the presence of vacant d orbital and more positive character of that metal ion. Complexes of Co(II) and Ni(II) with ampyrone and oxalate ion have been prepared and characterized by metal estimation, molar conductance,UV-visible spectra, IR-spectra, redox property (cyclic voltammetry) and biological activities. From the results of metal estimation and molar conductance, the general formula of the complex is $[M(L1)_4(X)]$ where M is Co(II) and Ni(II), L is ampyrone (monodentate) and X is oxalate ion (bidentate). The metal ligand ratio is 1:2:1 and it is non-electrolyte, neutral complexes. The magnetic moment and UV-visible spectral data of the complexes confirm the octahedral geometry around the metal ion. The results of IR spectra of the ligands and its complexes show the coordination atom is nitrogen of ampyrone and oxygen of oxalate ion. Redox property of Ni(II) complex from cyclic voltammeter exhibit quasi reversible one electron transfer reaction. The antibacterial and antifungal activities of ampyrone and its complexes were tested against E. coli, P. aeruginosa, K. Pnemonia and A. Niger (Fungus) by Agar well diffusion methods. The results indicate that the complexes are more active than the ampyrone.

Key Words: Ampyrone, Oxalate ion, Cyclic voltammeter, Antibacterial, Antifungal.

INTRODUCTION

Pyrazoles are the five member heterocyclic compounds. Many organic compounds contain the pyrazoles moiety. Pyrazoles and its derivatives are used as the antibiotic[1]. Ampyrone is one of the temperature reducing pyrazole derivatives. It has variety of applications in many fields such as analytical, biological and pharmacological[2]. Ampyrone itself act as a good antimicrobial and antipyretic, analgesics, anti-inflammatory and anticancer agents[3-5], with the combination of metal ions the biological activity should be enhanced. Spectral data revealed that the ampyrone is monodentate neutral organic ligand it can coordinate through nitrogen or oxygen atom. The oxalate ion is bidentate coordinate through the oxygen atom; both ligands are N or O donor. In the present study mainly aims at the preparation, spectral, redox and biological activities of Co(II) and Ni(II) complexes of ampyrone and oxalate ion.

MATERIALS AND METHODS

Metal nitrates: Cobalt nitrate and Nickel nitrate (AnalaR grade), Reagents and Solvents: DMSO, DMF, ethanol, methanol (AnalaR grade), Ligands: sodium oxalate (AnalaR grade) and ampyrone commercially available was purchased from Alfa Aesar Company. All the chemicals and reagents were used as such without further purification.

Instruments

Cobalt estimated by volumetrically (EDTA method) and nickel were estimated by gravimetrically (using DMG) after decomposing a known weight of the metal complexes with HNO_3, using the standard procedure. The molar conductance of 10^{-3} solutions of the metal complexes in CH_3CN was measured with Systronic Conductivity Bridge 304 at room temperature. The magnetic moment of the complexes were measured using a Lake Shore 7410 model Vibrating Sample Magnetometer (VSM) and the UV-Visible spectra of complexes were recorded on Varian make, Cary 5000 model UV-VIS-NIR Spectrophotometer. The IR spectra of the ligand and their complexes were recorded on a Shimadzu FT-IR spectrometer in 4000-400 cm^{-1} range with KBr pellet technique. The redox properties of Ni(II) complex was carried out using Princeton Make (MC-Tech, applied research) cyclic voltammogram in DMF solution (10^{-3}M) containing 0.1M tetrabutylammoniumtetrafluoroborates as supporting electrolyte. The three electrode systems consist of glassy carbon (working), platinum (counter or auxiliary) and calomel (reference) electrodes. The antibacterial and antifungal activities of ampyrone and its complexes were tested by Agar well diffusion method using Amikacin and Ketoconazole standard.

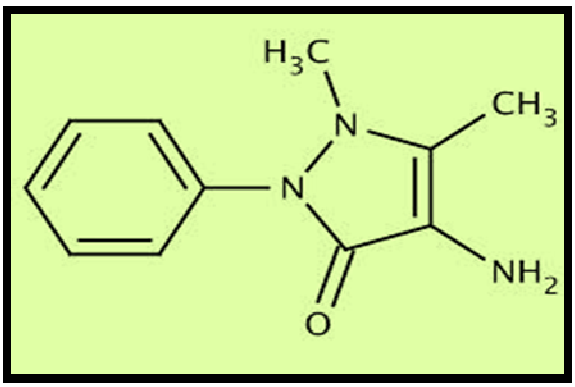

Figure-1

Structure of Ampyrone

Preparation of complex

Co(II) complex

Cobalt nitrate 1g dissolved in methanol, 4-aminoantipyrine 2.79g in ethanol was added in drops with constant stirring; the mixture was heated on a water bath for about 20 minutes. Then sodium oxalate 0.46 g in ethanol was added to the above solution and the whole mixture was heated on a water bath for about 30 minutes. The precipitated pink colour complex was filtered, washed with ethanol and dried.

Ni(II) complex

To a solution of nickel nitrate, 1 g in methanol, 2.79g of ampyrone in ethanol was added in drops with constant stirring. The mixture was heated on a water bath for about 30 minutes. Then 0.49g of oxalate in ethanol was added to the above mixture and heated on a water bath for about 45-50 minutes. The precipitated, pale green complex was filtered, washed with ethanol and dried.

RESULT AND DISCUSSION

Molar Conductance

The molar conductance of the complex in CH_3CN at 30°C lie in the low range indicates the non-electrolyte nature (1:0 type) of the complex. Comparisons of the measured molar conductance with that of a known ionic compound allows estimation of the number of ions produced in CH_3CN solution.[6]

Cyclic voltammogram

The reduction peak of Ni(II)/Ni(I) couple for the cadmium complex was observed in the potential range from Epa = 1.6v to Epc = 0.800v, the ΔEp values for the complex is 0.800v which corresponds to the quasi reversible one electron transfer reaction.[7]

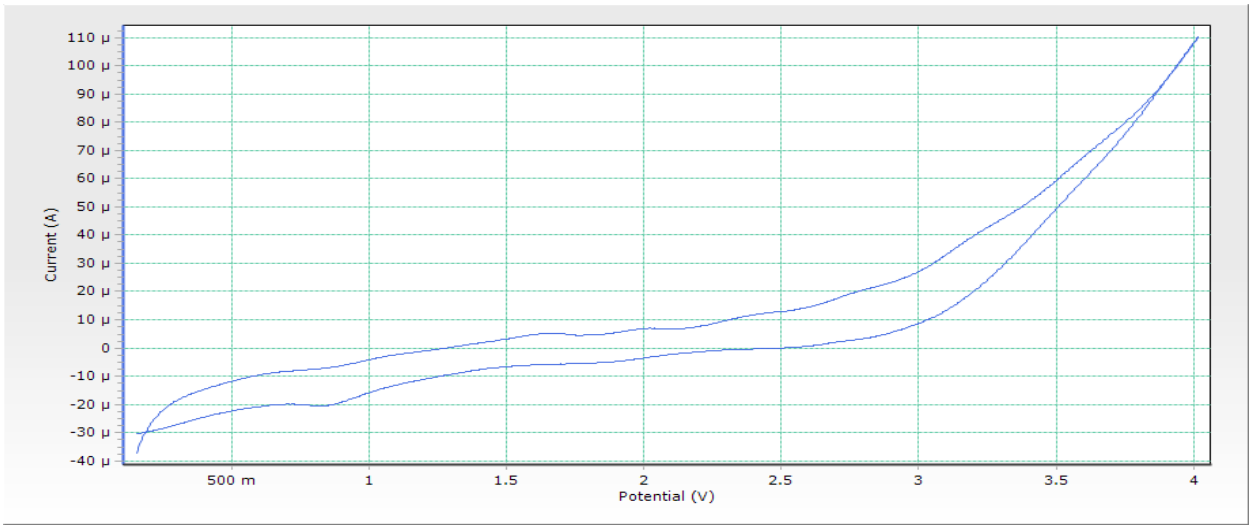

Figure-2

Cyclic voltammogram of Ni(II) complex

UV-Visible spectrum[8]

The Ni(II) complex exhibit three absorption band at 810nm, 620nm, 255nm. The energy level diagram for ligand field predicts three transition, These transitions suggest the distorted octahedral geometry around Ni(II). On the basis of theoretical and calculation the magnetic moment values of Ni(II) complex is 3.60BM which is also confirmed by the distorted octahedral geometry.

The electronic spectrum of Co(II) complex exhibits three bands of medium intensity observed at 610 nm, 440 nm and 230 they were assigned by the distorted octahedral geometry in addition to that the magnetic moment value is 2.95BM also confirmed the geometry.[9]

IR-Spectrum[10-11]

The infra red spectra of the free Ampyrone and oxalate ion were compared with those of the corresponding metal complexes. The free ligand ampyrone exhibited a strong band at 2914 cm^{-1} assignable to the ν(C-H) stretching frequency. The frequencies 1587 cm^{-1} and 1650 cm^{-1} may be assigned to ν(C=C) and ν(C=O) respectively.

The NH_2 frequency of Ampyrone at 3431 cm^{-1} is an asymmetric one and at 3325 cm^{-1} is a symmetric one. These two stretching frequencies are merged to give a broad band in the complexes, indicating the entry of Ampyrone into the coordination sphere. The ν(N-H) stretching frequency (3397cm^{-1}) shows irregular vibrational frequency in the complex which indicate the coordination of metal ion with N atom. The band observed at 1352 cm^{-1} is assigned to C-N stretching vibration, which is shifted to higher frequency range (1359cm^{-1}), confirming the coordination with N atom.

The oxalate ion frequencies in the complex observed at 802 cm^{-1} , 1607cm^{-1} , 1489 cm^{-1} can be assigned to ν(O-C=O), νa(C=O) and νs(C=O) stretching frequencies respectively which confirm the entry of oxalate ion into the coordination sphere.

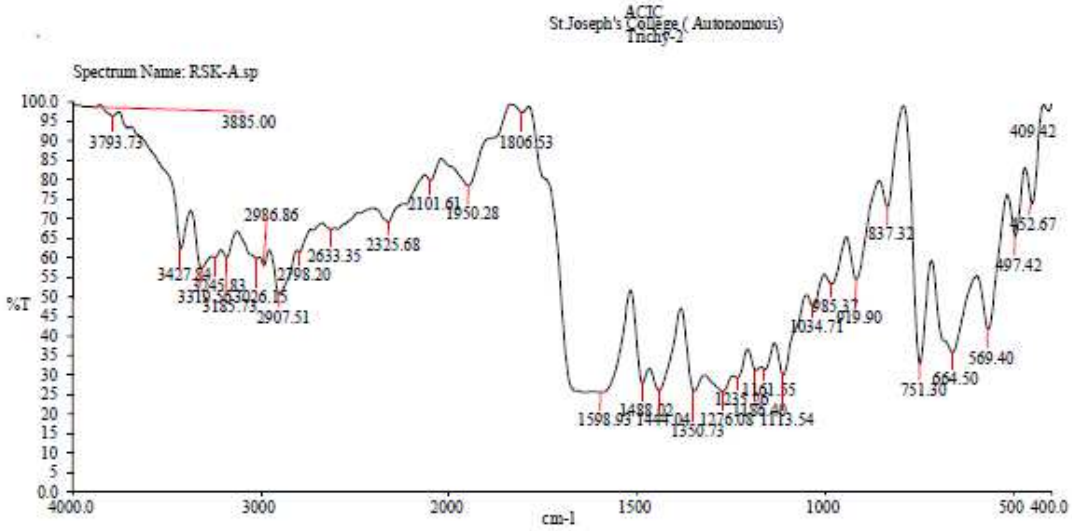

Figure-3 IR-SPECTRUM OF AMPYRONE

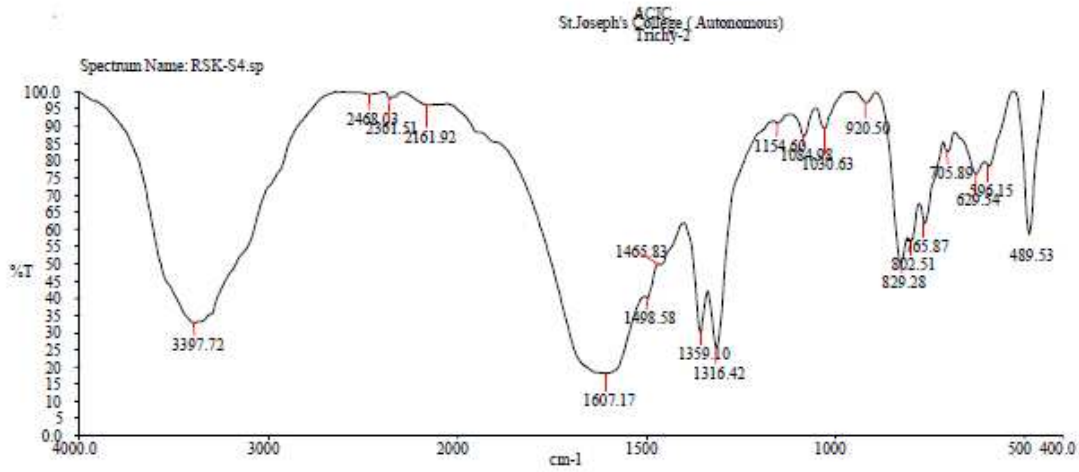

Figure-4 IR-SPECTRUM OF Co(II) COMPLEX

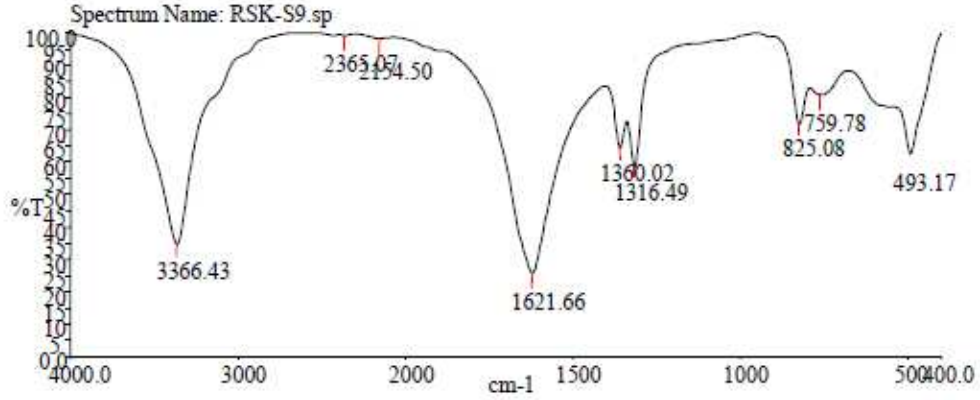

Figure-5 IR-SPECTRUM OF Ni(II) COMPLEX

Antibacterial and Antifungal Activities[12-13]

The antibacterial and antifungal activities of 4-aminoantipyrine and oxalate ion metal complex were tested against *E. coli, Klebsilla Pnemonia, A. Niger (Fungus) and P. aeruginosa* by the agar well diffusion method. The test solution was prepared in the DMSO solvent. Amikacin and Ketoconazole were used as standards for antibacterial and antifungal activities respectively. The results indicate that the complex is highly active for *Klebsilla Pnemonia, A. Niger (Fungus)* than the free 4-AAP and moderately active for *E. coli* and *P. aeruginosa*.

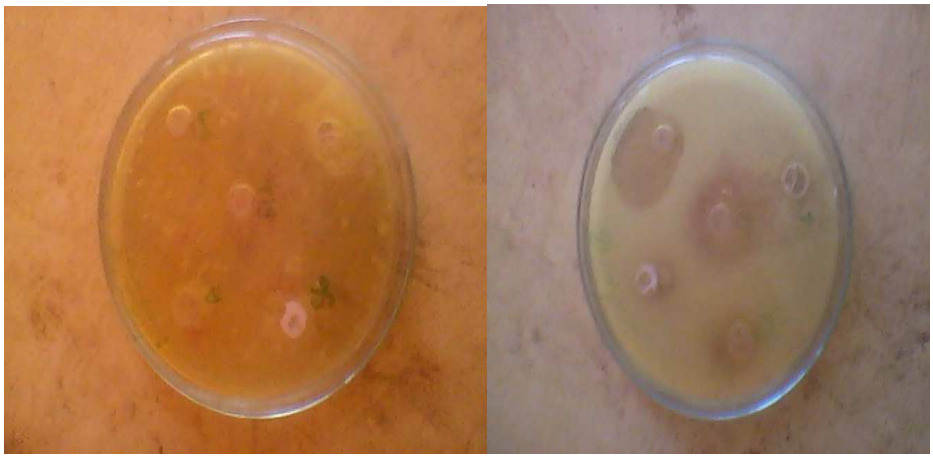

Figure-6
Zone of inhibition for *A.niger and E.coli*

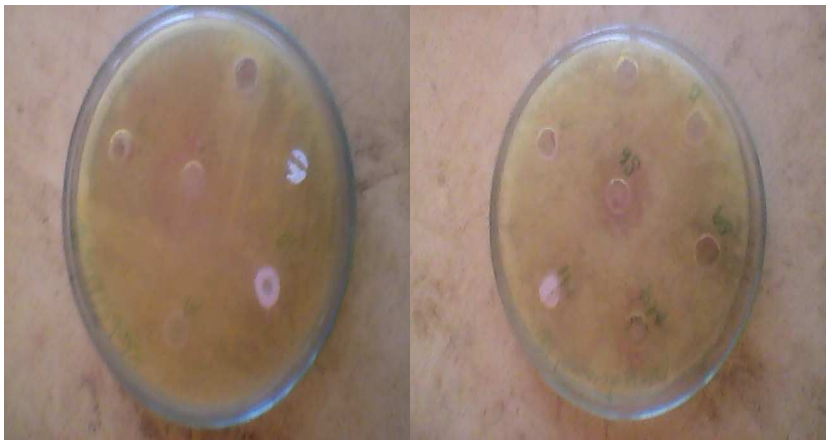

Figure-7
Zone of inhibition for *Klebsilla Pnemonia and P.aeruginosa*

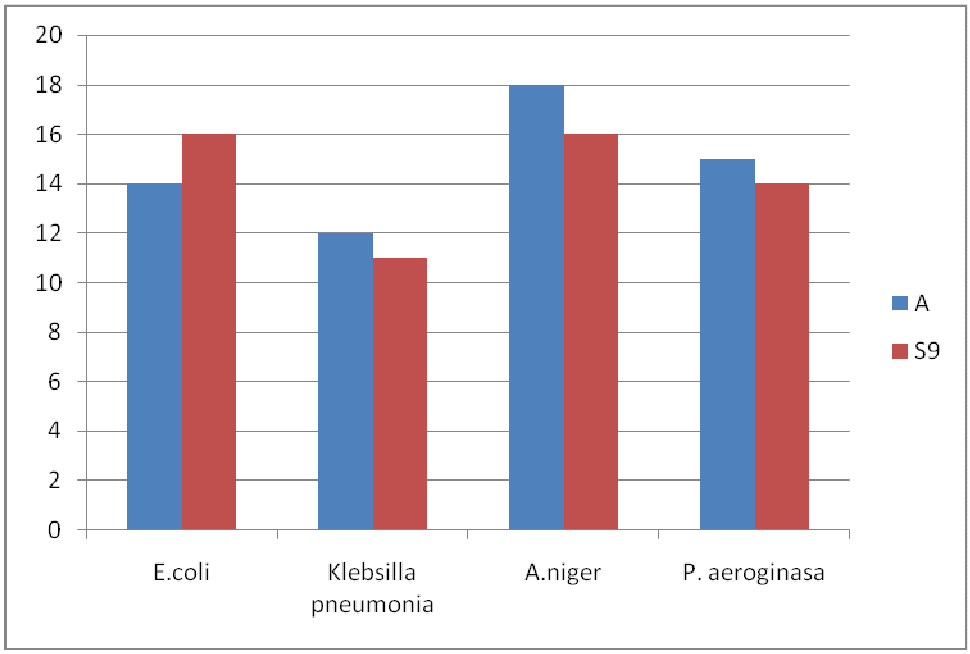

Figure-8
Comparative diagram of ampyrone and its complexes

CONCLUSION

In this paper the synthesis of Co(II) and Ni(II) complexes with ampyrone and oxalate ion were attempted, the distorted octahedral geometry was confirmed by various spectral studies. The stoichiometry composition and nonelctrolytic nature of the complex confirmed from the metal estimation and molar conductance. Quasi reversible one electron transfer reaction was confirmed by cyclic voltammetry study. The complexes are biologically active based on the results these compounds are **neutral, monomer, distorted octahedral geometry**. It has good biological activity.

REFERENCES

[1] Yogesh Kumar Vaghasiya, Rathish Nair, Mayur Soni, Shipra Baluja and Sumitra Chanda, *J. Serb. Chem. Soc.,* **2004**,69(12), 991.

[2] K. Rajasekar, T. Ramachandramoorthy and S. Balasubramaniyan, *Chem Sci Trans.,* **2013**,2(3),877-882.

[3] N. Raman, A. Sakthivel and K. Rajasekaran, *Mycobiology*, **2007**,35(3), 150.

[4] N. Raman, C. Thangaraj and S. Johnson raja, *Central European Journal of Chemistry*, **2005**,3(3), 537.

[5] N.Raman, A. Kulandaisamy and A. Shanmugasundaram, *Transition Metal Chemistry,* **2001**,26, 131.

[6] Paulmony Dharmaraj, Deivasigamani Kodimunthiri, Clarence. D. Sheela and Chappani S. Shanmuga Priya, *J. Seb. Chem. Soc.*, **2009**,74(8-9), 927.

[7] B. Anubama, M. Padmaja and C. Gyana Kumari, *E-Journal of Chemistry*, **2012**,9, 389.

[8] Pedro M.P.Santos, Alexandra M.M.Antunes, Joao Noronha, Eduara Fernandes and Abel. J.S.C. Vieira, European Journal of Medicinal Chemistry, **2010**,45,2258-2264,.

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

[10] M.M. El-ajaily, R.M. El-Ferjani and A.A. Maihub, *Jordan Journal of Chemistry,* **2007**,2, 287.

[11] Qian Wang, Ming-Jie Wu, En-Cui Yang, Xiu-Guang Wang and Xiao-Jun Zhao, *Journal of Coordination Chemistry*, **2007**,61(4), 595.

[12] Silvio Cunha, Shana M. Oliveira, Manoel T. Rodrigues Jr, Rodrigo M. Bastos, Jailton Ferrari, Cecilia M.A. De Oliveira, Lucilia Kato, Hamilton B. Napolitano, Ivovencato and Carlito Lariucci, *Journal of Molecular Structure,* **2005**,752(1-3), 32.

[13] E.H. Al-Tememe and R.M. Al-Hrashawy, *Bas. J. Vet. Res.,* **2010**,9(1), 163.