*Asian Journal of Chemistry* Vol. 22, No. 2 (2010), 978-982

# Synthesis, Characterization of Ru(II) Complexes of New Schiff Bases

K.P. BALASUBRAMANIAN* and V.V. RAJU
*Department of Chemistry, Gobi Arts and Science College, Gobichettipalayam-638 453, India*

The synthesis and characterization of six hexacoordinated Ru(II) complexes of the type [RuC1(CO)($EPh_3$)(B)(L)] (E = P or As; B = $PPh_3$, $AsPh_3$ or pyridine; L = monobasic bidentate Schiff base anion) are reported. IR, electronic, $^1$H NMR and $^{31}$P NMR spectral data are discussed. An octahedral geometry has been tentatively proposed for all theses complexes.

**Key Words: Schiff base, Ru(II) complexes.**

## INTRODUCTION

The azomethines were used as anticaner[1,2], tuberculostically[3,4], antiinflammatory[5], antiviral[6], anticatract[7], fungicidal[8], pesticidal[8], bactericideal[9], insecticidal[10], herbicidal[11] and growth regulating agents[12] and also found a place in the technological fields like automobile[13], electroplating[14], photography[15], polymer technology[16], paints and perfumes[17], textile and detergents[18] and environmental science[19].

The chemistry of organo metallic compounds of transition metals has long been a subject of much interest due to growing applications in the field of catalysis[20,21]. Ruthenium offers a wide range of oxidation states and the reactivity of the ruthenium complexes depend on the stability and interconvertibility of these oxidation states, which in turn depend on the nature of the ligand bound to the metal complexation of ruthenium by ligands of different types has thus been of particular interest[22,23].

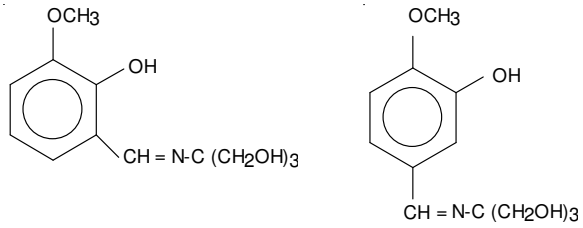
## EXPERIMENTAL

The starting complexes [RuHCl(CO)($PPh_3$)$_3$][24], [RuHCl(CO)($AsPh_3$)$_3$][25], [RuHCl(CO)($PPh_3$)$_2$(py)][26] and the ligands[27] were prepared according to the literature procedures.

**Preparation of new ruthenium(II) complexes:** To a solution of [RuHCl(CO)($PPh_3$)$_3$], [RuHCl(CO)($AsPh_3$)$_3$], [RuHCl(CO)($PPh_3$)$_2$(py)] (0.1 g, 0.08-0.01 mmol) in benzene (20 $cm^3$) the respective ligands (0.03-0.08 g, 0.08-0.1 mmol) were added. The resulting solution was concentrated to *ca.* 3 mL and the product was separated by the addition of the small amount of light petroleum (60-80 ºC). It was filtered and recrystallized form $CH_2Cl_2$/light petroleum (60-80 ºC) and dried in vacuum (yield = 70-85 %).

## RESULTS AND DISCUSSION

Light and air stable ruthenium(II) complexes of the general formula [RuCl(CO)($EPh_3$)(B)(L)] (E = P or As; L = monobasic bidentate anion) have been prepared by reacting [RuHCl(CO)($PPh_3$)$_3$], [RuHCl(CO)($AsPh_3$)$_3$] and [RuHCl(CO) ($PPh_3$)$_2$(py)] with the respective ligands in a 1:1 molar ratio in benzene.




(L1) (L2)

Structure of the ligands

$$[RuHCl(CO)(B)(EPh_3)_2] + HL \xrightarrow[\text{Reflux, 6 h}]{\text{Benzene}} [RuCl(CO)(EPH_3)(B)(L)] + H_2 + EPh_3$$

The analytical data obtained for these complexes (Table-1) agree well with the proposed molecular formulae in all of the above reactions, the ligand behave as mononegative bidentate ligands.

TABLE-1
ANALYTCIAL DATA OF NEW Ru(II) COMPLEXES

| Complex | m.p. (ºC) | Yield (%) | (Found) Calculated (%) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| $[RuCl(CO)(PPh_3)_2(L_1)]$ | 181 | 75 | 62.61 (64.73) | 5.65 (4.93) | 1.43 (1.49) |
| $[RuCl(CO)(PPh_3)_2(L_2)]$ | 176 | 85 | 62.82 (63.62) | 5.60 (5.17) | 1.48 (1.53) |
| $[RuCl(CO)(AsPh_3)_2(L_1)]$ | 157 | 70 | 59.08 (57.14) | 4.49 (3.43) | 1.45 (1.30) |
| $[RuCl(CO)(AsPh_3)_2(L_2)]$ | 159 | 70 | 59.60 (56.51) | 4.52 (4.53) | 1.42 (1.31) |
| $[RuCl(CO)(PPh_3)(py)(L_1)]$ | 172 | 80 | 68.46 (68.53) | 5.70 (5.38) | 4.43 (4.46) |
| $[RuCl(CO)(PPh_3)(py)(L_2)]$ | 179 | 75 | 68.57 (68.67) | 5.01 (5.07) | 3.69 (3.59) |

The IR spectra of the free ligands were compared with those of the new complexes in order to confirm the coordination of thiazolidinones to the ruthenium metal. The IR specutrum of the free ligands showed a band in the absorption due to ν(C=N) appears in the 1620-1600 $cm^{-1}$ region undergoes a negative shift by 5-25 $cm^{-1}$ in the spectra of the complexes indicating the coordination of azomethine to the metal[28]. A strong band which appeared in the spectra of the ligands around 1610 $cm^{-1}$ due to ν(C=O) completely dispperated and a new band was observed around 1570 $cm^{-1}$. In all the carbonyl complexes the band due to terminal C≡O group appeared 1944-1900 $cm^{-1}$. In addition to the above, the characteristic bands due to $PPh_3$ or $AsPh_3$ were also present in the expected region[29].

All the complexes are diamagnetic indicating the presences of ruthenium in +2 oxidation state in all the complexes. In the electronic spectra of all the complexes in $CH_2Cl_2$ three to four bands are appeared in the region 640-250 nm. The bands in the region 640-750 nm are assigned to the trasition $^1A_{1g} \rightarrow {}^3T_{1g}$ and the bands around 400-370 nm are due to $^1A_{1g} \rightarrow {}^3T_{2g}$ transition. The other bands in the region 320-250 nm are probably due to charge transfer transitions ($t_{2g} \rightarrow \pi^*$). The nature of the electronic spectra are similar to those observed for other octahedral ruthenium(II) complexes[30].

The ligand to metal bonding is further supported by $^{1}H$ NMR spectra. All the complexes showed signals in the 8.0-8.99 ppm range due to the phenyl protons, ligand and $PPh_3/AsPh_3$[31]. The azomethine proton signals in the complexes lie in the 8.0-8.65 ppm range. The peak due to the azomethine showed a high field shift compared to the free ligand after complexation with the metal ion indicating coordination through the azo methane nitrogen atom[32,33].

The $^{31}P$ NMR spectra of three complexes were recorded in order to confirm the presence of $PPh_3$ groups and to determine the geometry of the complexes appearance of a single around 23.75-28.82 in the spectrum of complexes confirmed the presence of magnetically equivalent phosphorous atoms suggesting that the two $PPh_3$ groups are *trans* to each other[33].

The *in vitro* antimicrobial screening of the ligands and their ruthenium complexes have been carried out against *Eschericha coli*, *Aeromonas hydrophila* and *Salmonella typhi* using a nutrient agar medium by disc diffusion method[34]. The results (Table-2) showed the complexes exhibit moderate activity against *Eschericha coli*, *Aeromonas hydrophila* and *Salmonella typhi*. The toxicity of ruthenium chelates increases on increasing the concentration[35]. The increase in the antimicrobial activity of the metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of the toxicity increase may be considered in light of Tweedys chelation theory[36]. Chelation considerable reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of central metal atom, which subsequently favours its permeation through the lipid layers of cell membrane. Furthermore, the mode of action of the compounds may involve formation of a hydrogen bond through the azomethine (>C=N) group with the active centers of cell constituents, resulting in interference the normal cell process. Though the complexes possess activity they could not reach the effectiveness

TABLE-2
ANTIMICROBIAL ACTIVITY OF LIGANDS AND RUTH NEW COMPLEXES

| | Diameter of inhibition zones (mm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *Escherichia coli* | | | *Aeromonas hychophila* | | | *Salmonella typhi* | | |
| Ligand/complex | 0.25% | 0.50% | 1.00% | 0.25% | 0.50% | 1.00% | 0.25% | 0.50% | 1.00% |
| $HL_1$ | 10 | 12 | 13 | 9 | 10 | 12 | 8 | 10 | 11 |
| $[RuCl(CO)(PPh_3)_2(L_1)]$ | 12 | 14 | 16 | 11 | 14 | 17 | 10 | 12 | 15 |
| $[RuCl(CO)(AsPh_3)_2(L_1)]$ | 11 | 13 | 15 | 10 | 11 | 13 | 10 | 12 | 14 |
| $[RuCl(CO)(py)(PPh_3)(L_1)]$ | 12 | 14 | 15 | 11 | 13 | 14 | 11 | 14 | 15 |
| $HL_2$ | 10 | 11 | 12 | 9 | 10 | 11 | 9 | 11 | 12 |
| $[RuCl(CO)(PPh_3)_2(L_3)]$ | 13 | 14 | 16 | 10 | 12 | 14 | 10 | 12 | 15 |
| $[RuCl(CO)(AsPh_3)_2(L_3)]$ | 12 | 15 | 16 | 10 | 11 | 13 | 10 | 12 | 14 |
| $[RuCl(CO)(py)(PPh_3)(L_2)]$ | 13 | 14 | 15 | 12 | 13 | 15 | 12 | 14 | 15 |
| Streptomycin | 22 | 23 | 28 | 21 | 27 | 29 | 29 | 21 | 25 |

of the standard drug streptomycin. The variation in the effectiveness of the different compounds against different organism depend either of impermeability of the cells or the microbe of difference in ribosome of microbial cells.

Based on the analytical and spectral (IR electronic, $^{1}H$ NMR and $^{31}P$ NMR) data, an octahedral structure has been tentatively proposed for all of the new ruthenium(II) complexes (Fig. 1).

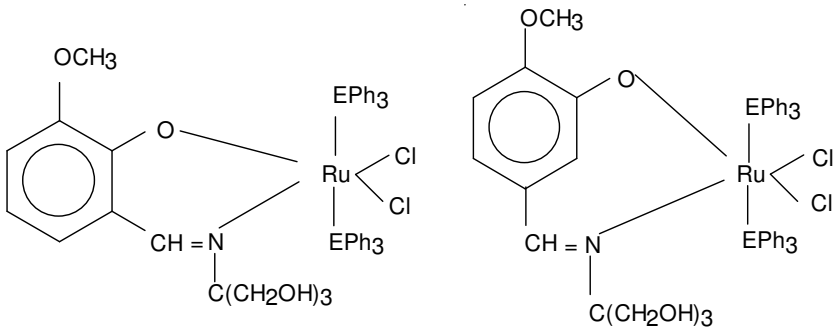



Fig. 1. Tentative structure of new Ru(II) Schiff base complexes

## ACKNOWLEDGEMENT

One of the authors (VVR) thanks the University Grants Commission, SERO, Hyderabad, India for the award of minor research project.

## REFERENCES

1. C. Kim, J. Lee and H.L. Young, *Korean J. Med. Chem.*, **2**, 64 (1992).
2. D.T. Chaudari and S.S.Sabnis, *Bull. Haffkine Inst*., **4**, 85 (1976).
3. L. Muslin, W. Roth and H. Erlenmeyer, *Helv. Chim. Acta*, **36**, 886 (1953).
4. L.F. Tresilova and I. Postovskn, *Ya Doklady Akad Nauk. USSR*, **114**, 116 (1957).
5. R. Nakquier, M. Crozet, P. Venella and M. Jose, *Tetrahedron Lett*., **26**, 5523 (1985).
6. Burr Anders and Hans Bundgard, *Arch Pharm. Chem. Sci. Ed.*, **15**, 76 (1987).
7. F. Elstner and F. Erich, Ger offen. DE, 3,617,711 (1987).
8. M.M.K. Emad, I.A. Chandnaya and Z.S. Novikova, *Vestn. Mosk Uni. Sci. Z. Khim*, **32**, 405 (1991).
9. M.A. Ali, C.M. Haroon, M. Nazimuddin, S.M. Mahbub-ul-Haque Majumder, M.T.H. Tarafder and M.A. Khair, *Transition Met. Chem*., **17**, 133 (1992).
10. W. Singh and D.C.M. Dash, *Pesticides*, **22**, 23 (1988).
11. A.I.P. Sinha and B. Manu, *Acta Cien. Ind.*, **14C**, 5 (1988).
12. V.A. Serznania, F.B. Kachuovskaya, N.G. Rozhknova, G.K. Smirnova and E.I. Andeeva, *Vestsi. Akad Navuk. BSSR Ser. Khim. Navok*, **1**, 116 (1986).
13. S. Omi, Y. Serzuki, H. Uco and H. Kunkiko, *Jpn. Kokai Tokkyo Koho. J.P*., **6**, 107 (1986).
14. P. Adalbert and E. Braig, *Ger. Offen. DE*, **4**, 141 (1992).
15. K. Shin, F. Tsuyoshi, Y. Micro, I. Satosh, A. Naka and Y. Tomda, *Eru. Pat. Appl. Ep. JP. Appl*., **78**, 736 (1996).
16. V. Mishra and D.S. Parmar, *J. Indian. Chem. Soc*., **72**, 811 (1995).
17. D. Mookherjee, Braja, W. Trenkle, Robert, Niconolas, Calderone-Fenn Ronald, US, 4, 853 (1989).

18. Manukian, K. Badrig, Walter, Huber and Ernst, *Gazz. Chim. Ital*., 120 (1990).
19. Hiroshi, Vchama and Tanno kyottiko, *Jpn, Kokai, Tokkyo Koho JP*, **4**, 0592661 (1993).
20. C. Aitken, J.F. Harrod and E. Samuel, *J. Org. Met. Chem*., **279**, C11 (1985).
21. A. Fochi and C. Floriani, *J. Chem. Soc., Dalton Trans*., 2577 (1984).
22. G. Das, R. Shukla, S. Mandal, R. Singh, P. K. Bharadwaj, J.V. Hall and K.H. Whitmire, *Inorg. Chem*., **36**, 323 (1997).
23. D.J. Jones, V.C. Gibson, S.M. Green and P.J. Maddox, *Chem. Commun*., 1038 (2002).
24. N. Ahmed, J.J. Levision, S.D. Robinson and M.F. Uttley, *Inorg. Synth*. **15**, 48 (1974).
25. R.A.S. Delgade, W.Y. Lee, S.R. Choi, Y. Cho and M.Y. Jun, *Transition Met. Chem*., **16**, 241 (1991).
26. K.P. Balasubramanian, S. Manivannan and V. Chinnusamy, *Ultra. Chem*., **4**, 15 (2008).
27. R. Srinivasulu and J. Sree Ramulu, *Acta Cien. Ind.*, **30C**, 181 (2004).
28. M.V. Kaveri, R. Prabhakaran, R. Karvembu and K. Natarajan, *Spectrochim. Acta*, **61A**, 2915 (2005).
29. R. Karvembu, S. Hemalatha, R. Praphakaran and K. Natarajan, *Inorg. Chem. Commun*., **6**, 486 (2003).
30. R. Karvembu and K. Natarajan, *Polyhedron*, **21**, 1721 (2002).
31. J.Y. Kim, M.J. Jun and W.Y. Lee, *Polyhedron*, **15**, 3787 (1996).
32. D. Chattaerje, A. Mitra and B.C. Roy, *J. Mol. Cat*., **161**, 17 (2000).
33. R. Prabhakaran, A. Geetha, M. Thilagavathi, R. Karvembu, V. Krishnan, H. Bertagnolli and K. Natarajan, *J. Inorg. Biochem*., **98**, 2131 (2004).
34. B.G. Tweedy, *Phytopathology*, **55**, 910 (1964).
35. S.C. Singhadon, N. Gupta and R.V. Singh, *Indian J. Chem*., **34A**, 733 (1995).
36. P.G. Lawrence, P.L. Harold and O.G. Francis, *Antibio. Chemother*., **5**, 1597 (1980).

(*Received*: 24 October 2008; *Accepted*: 7 October 2009) AJC-7933