

SCHIFF BASE LIGAND COMPLEXES OF TITANIUM (III), VANADIUM (III), RUTHENIUM (III), IRIDIUM (III) AND RHODIUM (III)

AKANKSHA SHARMA AND DR. RAJNISH SAXENA

Department of Chemistry, S.M. College, Chandausi (Sambhal)–202 412 (India)

RECEIVED : 16 March, 2016

A number of novel Schiff ligand complexes of type $\{M(LX)\}_2 X_2$ have been synthesized and characterized, where M = Ti (III) or V (III) or Ruthenium (III) or Iron (III) or Iridium (III) or Rhodium (III), L = 2, 6 diacetyl Pyridine bis (S-methyl isothiosemi-carbazone), X = cl. All the complexes have been found to have 1 : 1 stoichiometric composition. The complexes have been characterized by elemental analysis, IR, nmr spectral studies, determination of melting points and molar conductance measurements. IR spectral data show that the hydrogen bonding in these complexes is a dominant factor for their stability.

INTRODUCTION

Titanium (III), Vanadium (III), Ruthenium (III), Iron (III), Iridium (III), and Rhodium (III) complexes have biological importances. Transition metal complexes have been well investigated earlier. In this communication we taken the Schiff base ligands to investigate the co-ordination behaviour towards the above transition metals and also to study whether dominant factor for their stability.

EXPERIMENTAL

2, 6 diacetyl pyridine bis (S-methyl) isothiosemicarbazone and all the chemicals of AR grade or equivalent purity were used as such :

Preparation of metal complexes of Titanium (III), Vanadium (III), Ruthenium (III), Iron (III), Iridium (III) and Rhodium (III)

The warm solution of Ti (III) or V (III) or Ruthenium (III) or Iron (III) or Iridium (III) or Rhodium (III) metal salt was mixed with the freshly prepared solution of the ligand in (1 : 1) (mole) in absolute ethanol. The reaction mixture was refluxed 8-10 h with constant stirring. The product so formed was filtered, washed with cold ethanol followed by diethyl ether and dried in vacuo over fused calcium chloride.

Preparation of Ligand

{2, 6- diacetyl pyridine bis (S-methyl iso-thio-semicarbazone)} : 2, 6-diacetyl pyridine was dissolved in 10 cm³ of ethanol in a round bottom flask. To this was added freshly prepared ethanolic (0.1 M mol/10 cm³) solution of S-methyl thioisosemicarbazide. The mixture was refluxed at about 40°C for 3 Hrs. Creamish white precipitate was formed on

cooling in crushed ice for 1-2 Hr. It was filtered, washed with cold methanol. It was purified by recrystallization from ethanol and dried. The purity of the sample was established by TLC.

RESULTS AND DISCUSSION

Some physical properties of the ligand (2, 6 diacetyl pyridine bis {S-methylisothiosemicarbazone} and the metal complexes {M (LX)} X₂ obtained and listed in Table 1.

2, 6 diacetyl pyridine bis S-methylisothiosemicarbazone is a creamish white. The metal complexes are generally coloured, soluble in DMF and DMSO but insoluble in ethanol, methanol, ether, acetone, TMF, chloroform and water.

Molar Conductance : Molar conductance of all complexes were measured in methanol at 27°C at a concentration of 10³ M. The values are given in Table-1.

The value of about 90-150 Ohm⁻¹ cm²mole⁻¹ appears where as ideally molar conductance of a neutral complex should be zero.

1. Determination of melting points :

The melting points were determined by open capillary method & are given in Table 1

2. Elemental Analyses :

C, H, N were estimated by microanalyses where as metal sulphur & chloride were estimated gravimetrically in the lab. The results are given in table 1

3. Magnetic susceptibility :

It was determined by gouy's balance & the magnetic moments were calculated from the value of magnetic susceptibility using the formula.

$$\chi_{\text{eff}} = 2.84 (X_M T)^{1/2}$$

X_M = Corrected molar susceptibility

T = absolute temperature °K.

The sample tube was calibrated with CuSO₄. 5H₂O.

These studies were carried out at Deptt. of Chemistry, Bareilly College, Bareilly

The values of magnetic moments are given in table 1.

Infrared Spectra : The Infrared Spectra of the ligand was compared with that of the V (III) or Ti (III), Ru (III), Fe (III), IR (III) and Rh (III) complexes. The pyridine ring vibrates, most affected by nitrogen of pyridine in coordination with a metal atom are pyridine ring deformation and out plane deformation (3). These vibrations appear at 1580, 620 and 140 cm⁻¹ respectively in the spectrum of the free ligands. In plane deformation and out plane deformation bands show an upward shift of 25-40 cm⁻¹ respectively upon coordination with the metal (4). Although pyridine ring deformation band is less sensitive coordination, the ^u(M-N_{p4}) vibration (5) located at 260 cm⁻¹ verified the coordination of pyridine nitrogen with metal ion. Medium band at 1610 cm⁻¹ has been assigned to (NH₂) groups of isothio semi carbozidemoietis and showed downward shift due to involvement of NH₂ (Isothioamide group) with metal atom in coordination.

The ligand showed two bands at 1640 and 1620 cm⁻¹, assignable to azomethine linkage of the isothiosemicarbazide (6, 7), -N= C (SCH₃) NH₂ and the iso-thiosemicarbazide linkage C₅H₃N-(CH₃) C=N, formed by condensation of isothiosemicarbazide with 2, 6 diacetyl pyridine, band due to isothiosemicarbazide (-N= C (SCH₃) NH₂) fragment remained at the

same position but the $C_5H_3N-(CH_3)C=N-$ linkage shifted to the lower frequency by 20 cm^{-1} in their spectrum of the complex. The appearance of a weak band $\nu(C=N)$ is in accord with other observations (8). This was further confirmed by the presence of non ligand band at 380 cm^{-1} assignable to $\nu(V-N)$ band. This indicates involvement of only one of the azomethine linkage in coordination (9). The new band appearing in the ir spectrum of the complex at 320 cm^{-1} may be assigned to $\nu(M-Cl)$.

These ir assignments suggested quinquedentate nature of the ligand (9), which seems to have coordination through pyridine nitrogen, two azomethine nitrogen atoms and two isothioamide nitrogen atoms

STRUCTURE AND BONDING

On the basis of elemental analysis, determination of melting points, IR, nmr spectral measurements suggests the probable structure for these complexes (fig. 1)

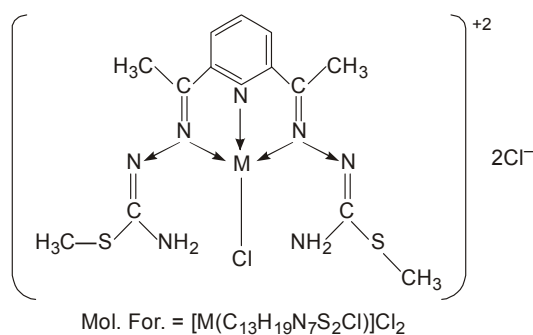


Fig. 1

REFERENCES

1. Kakos, G.A., Winter, G., *Aust J. Chem.*, **2**, 48 (1977).
2. Machin, D.J. and Murray, K.S., *J. Chem. Soc.*, **A**, 1498 (1961).
3. Gudasi, K.B., Patil, S.A., Vadavi, R.S., Shenoy, R.V., Nethaji, M. and Bligh, S.W.A., *Inorg Chem Acta*, **359**, 3229 (2006).
4. Novakovic, S.B., Bogdanovic, G.A., Leovac, V.M., *Polyhedron*, **25**, 1096 (2006).
5. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc. New York (1997).
6. Bat, T., Ulkuseven, B., *Trans Met Chem*, **29**, 880 (2004).
7. Kaur, P., Sarangal, A., Mc Innes, E and Robinson, W.T., *J. Coord. Chem*, **57**, 797 (2004).
8. Brown, C.A., Kaminsky, W., Claborn, K.A., Goldberg, K.I. and West, Dx, *J. Brazil Chem Soc.*, **13**, 10 (2002).
9. Sharma, Vinod K. and Srivastava, Ankita, *Indian Journal of Chemistry*, Vol. **46 A**, pp 1963-68 (2007).
10. Swamy, S.J., Reddy, A. Dhama and Bhoskav, K., *Indian Journal of Chemistry*, **40A**, pp 1166-1171 (2001).
11. Maurya, R.C., Verma, R. and Shukla, B., *Indian J. Chem*, **38A**, 730 (1999).
12. Maurya, R.C., Pandey, H. Singh and Singh, J., *Indian J. of Chemistry*, **40 A**, pp 1053-63 (2001).
13. Dey, Kamalendu and Chakraborty, Kartick, *Indian Journal of Chemistry*, **38A**, pp 381-384 (1999).
14. Brown, C.A., Kaminsky, W., Claborn, K.A., Goldberg, K.I. and West, Dx, *J. Brazil Chem. Soc.*, **13**, 10 (2002).
15. Natrajan, C., Sheela, C.D. and Athappan, P.R., *Indian Journal of Chemistry*, **30A**, pp. 357-362 (1991).

