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Short Communication

Gravimetric Estimation of Metals in Schiff Base Metal Complexes

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ABSTRACT

Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperatures. The activity is usually increased by complexation therefore to understand the properties of both ligands and metal can lead to the synthesis of highly active compounds.

Keywords: Ligands, Schiff base, Transition metals, Cobalt.

INTRODUCTION

Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate. One of the most important types of catalytic mechanism is the biochemical process which involves the condensation of a primary amine in an enzyme usually that of a lysine residue, with a carbonyl group of the substrate to form an imine, or Schiff base. Ugras et al [1] have reported the synthesis, complexation, antifungal and antibacterial activity studies of a new macro cyclic Schiff base. Preparation, physical characterization and antibacterial activity of Ni (II) Schiff base complex was reported by Morad et al [2]. Elzahany et al [3] have synthesized some transition metal complexes with Schiff bases derived from 2- formyl indole, salicylaldehyde and N-amino Rhodamine. The Schiff base ligands were characterized by elemental analysis, IR, Mass, ^{1}H NMR and electronic spectra. Synthesis and pharmacological studies of novel Schiff bases of 4-Hydroxy 6-carboxyhydrazino benzofuran was reported by Gopal Krishna Rao et al. [4]

Metal complexes of Schiff base derived from 2-thiophene carboxaldehyde and 2-aminobenzoic acid (HL) and Fe(III) or Co(II) or Ni(II) or O_2(II) showed a good antibacterial activity against Escherichia coli, Pseudomonas aeruginosa and Staphylococcus pyogenes. Fe(III), Cu(II), Zn(II) and UO_2(II) complexes caused inhibition for E. coli. The importance of this lies in the fact that these complexes could be applied fairly in the treatment of some common diseases caused by E. coli. However, Fe(III), Co(II), Cu(II), Zn(II) and UO_2(II) complexes were specialized in inhibiting Gram-positive bacterial strains (Staphylococcus pyogenes and P. aeruginosa). The importance of this unique property of the investigated Schiff base complexes lies in the fact that, it could be applied safely in the treatment of infections caused by any of these particular strains [5].

Schiff base complexes of Co(II), Ni(II), Cu(II) and Zn(II) incorporating indole-3-carboxaldehyde and m-aminobenzoic acid were screened by disc diffusion method. The activity order of the synthesized compounds is as follows: Cu(II) > Co(II) > Ni(II) > Zn(II) > Ligand. The higher activity of the metal complexes may be owing to the effect of metal ions on the normal cell membrane. Metal chelates bear polar and nonpolar properties together; this makes them suitable for permeation to the cells and tissues. In addition, chelation may enhance or suppress the biochemical potential of bioactive organic species [6]. The metal complexes of Cu(II), Ni(II) and Co(II) with Schiff bases of 3-(2-hydroxy-3-ethoxybenzylidene amino)-5-methyl isoxazole and 3-(2-hydroxy-5-nitroben-zylidene amino)-5- methyl isoxazole which were obtained by the condensation of 3-amino-5-methyl isoxazole with substituted salicylaldehydes were screened against Aspergillus niger and Rhizoctonia solani. The ligands presented here and their transition metal complexes gave better results against the growth of fungi. It is found that the activity increases upon coordination. The increased activity of the metal chelates can be explained on the basis of chelation theory [7,8]. The orbital of each metal ion is made so as to overlap with the ligand orbital. Increased activity enhances the lipophilicity of complexes due to delocalization of π-electrons in the chelate ring [9]. In some cases, increased lipophilicity leads to breakdown of the permeability barrier of the cell [10,11]. The results of anti-fungal screening, indicate that Cu(II) complexes show more activity than the other complexes. These results may be due to higher stability constant of the Cu(II) complexes than the other complexes.

MATERIALS AND METHODS

Preparation of complexes: Ligands used in preparing Metal Complexes are glyoxalal-o-aminophenol, glyoxalal-m- aminophenol, glyoxalal-o-aminobenzoic acid, glyoxalal-o aminothiol and glyoxalal-phenyl hydrazine.

Cobalt complexes: The aqueous solution of Co(II) nitrate hexahydrate was taken in the 500mL beaker and heated at 60-80°C. The alcoholic solution of the ligand was added in 1:2 molar ratio, the contents were treated by gradual addition of water. Black, blackish green and brown precipitates of the chelates were separated and the complexes were filtered, washed repeatedly with water and dried in oven at 100 -110°C

Nickel complexes: An aliquot containing aqueous Ni(ll) solution was taken in 500 mL beaker and heated for half an hour. The red solution of the ligand (the solution of ligand in ethyl alcohol and ammonia in 1:2 v/v) was added slowly into the solution of metal ion.Yellow chelates were precipitated. The chelates were heated for half an hour and filtered, washed repeatedly with water and dried in electrical oven at 120-130°C as yellow solid.

Cu (II) complexes: Copper (II) sulphate was dissolved in water and the solution was taken in 500 mL distillation flask. The alcoholic solution of the ligand was added in 1:1 molar ratio. The mixture was refluxed for half an hour over water bath and then whole of the liquid contents were distilled until green solid complex was obtained. The complexes were washed repeatedly with water and alcohol and dried in an electrical oven at 120°C.

Ru (III) complexes: The aqueous solution of Ru (III) chloride was taken in the beaker and heated at 50-70°C. Alcoholic solution of the ligand was added in 1:2 molar ratio. The contents were treated by gradual addition of water. Brown, reddish brown precipitates of chelates were separated. The complexes were filtered, washed repeatedly with water, and dried in oven at 80°C.

Zr (lV) complexes: An aliquot containing Zirconium nitrate solution was taken in 500 mL beaker and the pH of the solution was maintained between 4.0 - 5.5 using acetate buffer. The alcoholic solution of the Schiff base having ‘1% (w/v) NaOH was then added in 1:2 molar ratios. Yellow, brown, orange precipitates were obtained. The precipitates were heated on steam bath at 60°-70°C for half an hour, filtered, washed repeatedly with water, alcohol and finally with ether and dried in electrical oven at 100 to 110°C.

Pd (II) complexes: The aqueous solution of Palladium chloride was taken in 500 mL beaker and the alcoholic solution of the ligand was added in 1: 1 molar ratio. The contents were heated at 70-80°C for half an hour over water bath upto the removal of alcohol. Brown precipitates of Palladium (II) complexes were obtained. The chelates were filtered, washed repeatedly with water, and dried in vacuo. Yellow, brown precipitates were obtained. These chelates were filtered, washed repeatedly with water, and dried in vacuo at 100°C.

UO_2 (VI) complexes: An aliquot containing UO_2 (VI) solution was taken in 500 mL beaker and the pH of the solution was maintained in between 3.0 - 6.0, using acetate buffer. The 1% (w/v) alkaline solution of the ligands was added in 1:1 molar ratio. Yellow, orange precipitates of dioxouranium chelates were obtained. The precipitates were then heated on steam bath at 60-70°C for half an hour, filtered and washed repeatedly with water, alcohol and finally with either and then dried in vacuo.

RESULTS AND DISCUSSION

Estimation of Cobalt (II) as CoO: The organo cobalt compound was treated with few drops of conc. HNO_3 at low temperature, ignited and then weighted as CoO.

Table 1: Gravimetric Estimation of Co (II) with Some Schiff Base and Molar Ratio

S. NO.	Schiff base (g)	$Co(NO_3)_2\ 6H_2O$ (g)	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		$Co(Gly\text{-}OAP)_2$	
	0.35	0.67	0.76	1:2
2.	(Gly-MAP)		$Co(Gly\text{-}MAP)_2$	
	0.34	0.67	0.76	1:2
3.	(Gly-OABA)		$Co(Gly\text{-}OABA)_2$	
	0.39	0.67	0.87	1:2
4.	(Gly-OAT)		$Co(Gly\text{-}OAT)_2$	
	0.36	0.67	0.82	1:2
5.	(Gly-Ph.hydrz)		Co(Gly-Ph.hydrz)2 $2H_2O$	
	0.32	0.67	0.84	1:2

Estimation of Ni (II) as dimethyl glyoximate: 0.3 g of organo nickel compound was first fused with conc. HNO_3 and dissolved nearly in 200 mL of water. The temperature was maintained at 70-80°C where a slight excess of dimethyl glyoxime reagent was added followed by regular stirring to get the precipitate. The contents were allowed to stand on a steam bath for nearly 30 min to settle the Scarlet red precipitate. The precipitate after an 1h was separated by filtering through already heated and weighed sintered glass crucible. The precipitate was washed with cold water and dried at 110-120°C for about 45-50 min. The drying was repeated until constant weight was reached.

Table 2: Gravimetric Estimation of Ni (II) with Some Schiff Base and Molar Ratio

S.NO.	Schiff base (g)	$NiSO_4.7H_2O$	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		$Ni(Gly\text{-}OAP)_2$	
	0.34	0.56	0.76	1:2
2.	(Gly-MAP)		$Ni(Gly\text{-}MAP)_2$	
	0.35	0.56	0.75	1:2
3.	(Gly-OABA)		$Ni(Gly\text{-}OABA)_2$	
	0.38	0.56	0.87	1:2
4.	(Gly-OAT)		$Ni(Gly\text{-}OAT)_2$	
	0.36	0.56	0.82	1:2
5.	(Gly-Ph.hydrz)		Ni(Gly-Ph.hydrz)2 $2H_2O$	
	0.32	0.56	0.83	1:2

Estimation of Copper as Cuprous thiocyanate: 0.4 g of organo copper compound was first ignited with concentrated nitric acid and was dissolved in 50 mL of water. A few drops of dilute hydrochloric acid and slight excess (about 20-30 mL were required) of freshly prepared saturated sulphurous acid solution was added. The solution was heated nearly to boiling and freshly prepared 10% ammonium thiocyanate solution was gradually added with the help of a burette until present in light excess with constant stirring. A white precipitate of cuprous thiocyanate was obtained. The contents were allowed to stand overnight and filtered through sintered glass crucible. The precipitate was washed ten to fifteen times with cold solution prepared by adding I ml. of a 1% solution of ammonium thiocyanate in 100 ml: of water and 5-6 drops of saturated sulphurous acid solution and finally several times with 20% alcohol to remove ammonium thiocyanate. The precipitate was dried to constant weight at 110-120°C as CuCNS.

Table 3: Gravimetric Estimation of Cu(II) with some Schiff Base and Molar Ratio

S.NO.	Schiff base (g)	$CuSO_4.5H_2O$	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		Cu(Gly-OAP)H_2O	
	0.35	0.50	0.47	1:2
2.	(Gly-MAP)		Cu(Gly-MAP)H_2O	
	0.34	0.50	0.75	1:2
3.	(Gly-OABA)		Cu(Gly-OABA)H_2O	
	0.39	0.50	0.54	1:2
4.	(Gly-OAT)		Cu(Gly-OAT)H_2O	
	0.36	0.50	0.52	1:2
5.	(Gly-Ph.hydrz)		Cu(Gly-Ph.hydrz)$_2$ $2H_2O$	
	0.32	0.50	0.77	1:2

Estimation of Ru(III):

Table 4: Gravimetric Estimation of Ru(III) with some Schiff Based and Molar Ratio

S.NO.	Schiff base (g)	$RuCl_2$ (g)	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		Ru(Gly-OAP)$_2$	
	0.34	0.42	0.86	1:2
2.	(Gly-MAP)		Ru(Gly-MAP)$_2$	
	0.34	0.42	0.86	1:2
3.	(Gly-OABA)		Ru(Gly-OABA)$_2$	
	0.38	0.42	0.97	1:2
4.	(Gly-OAT)		Ru(Gly-OAT)$_2$	
	0.36	0.42	0.93	1:2
5.	(Gly-Ph.hydrz)		Ru(Gly-Ph.hydrz)$_2$ $2H_2O$	
	0.32	0.42	0.93	1:2

Estimation of Zirconium (IV) as ZrO_2: Zirconium was estimated by either of the following methods

(a) The organozirconium compound was treated with a few drops of conc. HNO_3 at low temperature, ignited and then weighed as ZrO_2

(b) In those cases where spurting take place, the sample was first dissolved in dilute nitric acid and then the metal precipitated as hydroxide. The precipitate was filtered, washed and then ignited to $Zr0_2$ in silica crucible.

Table 5: Gravimetric Estimation of Zr (IV) with some Schiff Base and Molar Ratio

S.NO.	Schiff base (g)	$Zr(NO_3)_4$ $5H_2O$(g)	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		Zr(Gly-OAP)$_2$	
	0.35	0.85	0.82	1:2
2.	(Gly-MAP)		Zr(Gly-MAP)$_2$	
	0.34	0.85	0.82	1:2
3.	(Gly-OABA)		Zr(Gly-OABA)$_2$	
	0.38	0.85	93	1:2
4.	(Gly-OAT)		Zr(Gly-OAT)$_2$	
	0.36	0.85	0.88	1:2
5.	(Gly-Ph.hydrz)		Zr(Gly-Ph.hydrz)$_2$ $2H_2O$	
	0.32	0.85	0.89	1:2

Estimation of Palladium with Dimethyl Glyoxime: 0-3 of the chelate compound was first ignited with conc. nitric acid and dissolved in 100 mL of water having 0.25 N hydrochloric acid A 1% solution of dimethyl glyoxime in 95% alcohol was added at room temperature 2-5 mLof the reagent for every 10 g of palladium was used. The solution was allowed to stand for 1h and then filtered through a weighed sintered glass crucible. The orange yellow precipitate of palladium dimethyl glyoximate was thoroughly washed first with cold water and then with hot water It was dried at 110°C to constant weight.

Table 6. Gravimetric Estimation of Pd (II) with some Schiff Base and Molar Ratio

S.NO.	Schiff base (g)	$PdCl_2.2H_2O$ (g)	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		Pd(Gly-OAP)$_2$ H_2O	
	0.35	0.42	0.56	1:1
2.	(Gly-MAP)		Pd(Gly-MAP)$_2$ H_2O	
	0.34	0.42	0.56	1:1
3.	(Gly-OABA)		Pd(Gly-OABA)$_2$ H_2O	
	0.38	0.42	0.62	1:1
4.	(Gly-OAT)		Pd(Gly-OAT)$_2$ H_2O	
	0.36	0.42	0.59	1:1
5.	(Gly-Ph.hydrz)		Pd(Gly-Ph.hydrz)$_2$	
	0.32	0.42	0.85	1:1

Estimation of Uranium as UO_2: 0 3 g of organo uranium compound was first fused with concentrated nitric acid to convert as uranyl nitrate. The fused mass was dissolved in 1-2% acetic acid solution,5 0 g of A R ammonium acetate was added and heated to boiling, followed by adding 4% oxime solution drop wise with regular stirring. The whole mass was heated on a boiling water bath for 5-10 min. It was allowed to cool and filtered through a quantitative filter paper, washed several times with hot water and then with cold water. The precipitate was ignited and finally weighed as $U_3\ O_8$.

Table 7. Gravimetric Estimation of UO_2 (VI) with Some Schiff Base and Molar Ratio

S.NO.	Schiff base (g)	$UO_2(NO_3)_26H_2O$(g)	Solid complex yield (g)	Molar Ratio
1.	(Gly-OAP)		UO_2(Gly-OAP)$_2$ H_2O	
	0.34	1.00	0.89	1:1
2.	(Gly-MAP)		UO_2(Gly-MAP)$_2$ H_2O	
	0.35	1.00	0.87	1:1
3.	(Gly-OABA)		UO_2(Gly-OABA)$_2$ H_2O	
	0.38	1.00	0.95	1:1
4.	(Gly-OAT)		UO_2(Gly-OAT)$_2$ H_2O	
	0.36	1.00	0.92	1:1
5.	(Gly-Ph.hydrz)		UO_2(Gly-Ph.hydrz)$_2$	
	0.32	1.00	1.10	1:1

Estimation of Sulphur: Sulphur content of ligands and their metal complexes were estimated by Messenger's method.

CONCLUSIONS

Transition metal complexes containing Schiff bases have been of much interest over the last years, largely because of its various applications in biological processes and potential applications in designing new therapeutic agents.

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