



Transition Metal Complexes of 5-bromo Salicylaldehyde-2-furoic acid hydrazide; Synthesis and Characterisation

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ABSTRACT

A series of transition metal complexes of the ligand 5-bromo salicylaldehyde-2-furoic acid hydrazide have been prepared using Ti(III), Mn(III), V(III), Co(III), Fe(III), Ru(III) and Rh(III). The complexes have been characterized by elemental analyses, melting points, molar conductance, magnetic susceptibility measurement, electronic and infra red spectral studies. Based on these studies octahedral structures have been proposed for these complexes. The ligand has behaved in dibasic tridentate manner. The I.R. spectra of the complexes revealed non-participation of furan ring oxygen in coordination with the metal ions.

Key words: Furan ring, Coordination, Octahedral & Transition metal.

INTRODUCTION

The Coordination compounds derived from Schiff bases with transition metals have been studied with wide scope of their applications. It has emerged as a separate branch of coordination chemistry. The interest of the chemists in this field is developed due to novel structural features of these complexes and their utility in biological processes¹⁻⁷. The Coordination compounds of aryl hydrazones have been reported to act as inhibitor⁸. A survey of chemical literature indicated that few reports have appeared on the synthesis and characterization of metal complexes of salicylaldehyde-2-furoic acid hydrazide and its metal complexes, which undergoes to Keto-enol tautomerism. The present paper deals with the coordinating abilities of this

ligand which may lead to varied bonding and stereochemical behavior with different metal ions like Ti(III), Mn(III), V(III), Co(III), Fe(III), Ru(III), Rh(III).

MATERIAL AND METHODS

Ti(III) chloride was prepared in the laboratory by standard method while all other metals like Mn(III) chloride, V(III) chloride, Co(III) chloride, Fe(III) chloride, Ru(III) chloride and Rh(III) chloride were purchased from Loba Chemicals and used as such. 5-bromo salicylaldehyde (Merck) and 2-furoic acid hydrazide (Aldrich) were procured and used as such. The solvent like methanol, ethanol, DMSO, & DMF. Ethanol was double distilled before use. All other solvents were used as procured.

Synthesis of schiff base

A ethanolic solution of 5-bromo salicylaldehyde (1.005gm, 0.005mol in 10 cm³) was added to an ethanolic solution of 2-furoic acid hydrazide (0.63g, 0.005 mol in 10 cm³) and the mixture was refluxed on a water-bath for 5h. The excess of solvent was partially evaporated under a current of air and the white precipitate was separated by filtering under reduced pressure. It was washed with EtOH and crystallized from EtOH. The compound was dried in vacuum at room temperature over silica gel. The purity of the ligand was checked by T.L.C.

Preparation of metal complexes

The solution of metal salt was added drop by drop with constant stirring to the solution of the ligand until complete precipitation. The precipitate was filtered, washed with ethanol and dried in vacuum desiccator. This operation was carried in glove bag under the atmosphere of dry nitrogen gas for the preparation of Ti(III) and V(III) complexes while all other complexes were prepared in the open atmosphere.

Characterization of the ligand and metal complexes

The ligand and its metal complexes were subjected to elemental analyses for C, H and N, while metals were estimated gravimetrically in the laboratory. The melting points were determined by open capillary method and are uncorrected. The molar conductance was determined by Systronics (Model 30S) conductivity bridge in DMF at 25°C and 10⁻³M dilution. Magnetic susceptibility was determined by Gouy's method, using CuSO₄·5H₂O as calibrant. The electronic spectra of the complexes were recorded using Backmann-DU spectrophotometer. The IR spectra of the complexes were recorded in KBr phase at CDRI, Lucknow.

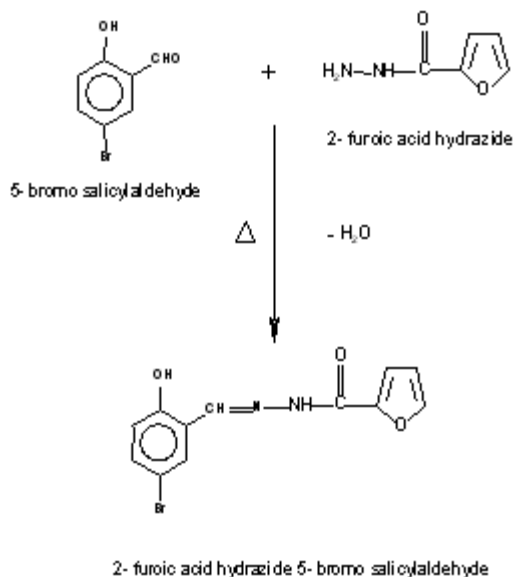
RESULTS AND DISCUSSION

The analytical data indicate that the M:L stoichiometry is 1:1 in all complexes. All complexes are insoluble in water and common non-coordinating solvent but are soluble in coordinating solvent like DMF and DMSO. The vast difference in melting points of the ligand and its complexes indicated their formation. The determination of molar

conductance suggested 1:1 electrolytic nature for all the complexes.

I.R. Spectra

The Schiff base exhibits the (C=O) at 1640 cm⁻¹ and this band is absent in the spectra of the complexes indicating the destruction of the carbonyl group due to the stabilization of the anion by



The ligand under goes Tautomerism.

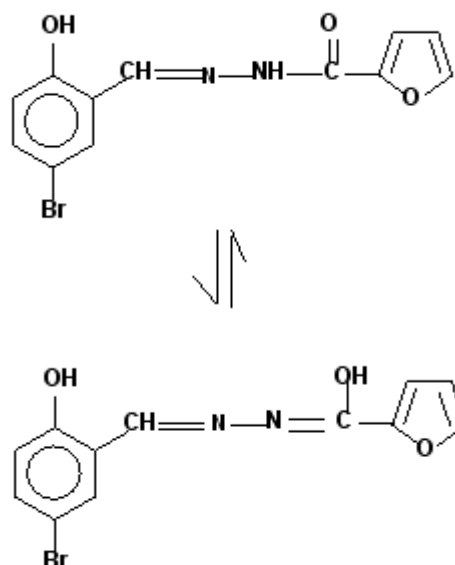


Table 1: Characterization of ligand and complexes

S. No.	Name and Molecular formula of the ligand (L) and complexes	Colour	M.P. %	Elemental Analysis			Magnetic Moment (B.M.)	Molar Conductance in DMF (Ohm ⁻¹ cm ² mol ⁻¹)	important peaks in I.R. Spectra			
			C	H	N	M		C=O	-C=N	-C-O	½-C-O-C (furan)	
1. (L)	2-furoic acid hydrazide 5-bromo salicylaldehyde, C ₁₂ H ₉ N ₂ O ₃ Br	White	130	46.60 (46.38)	2.91 (2.91)	9.06 (9.04)	-	-	1640	1620 cm ⁻¹ cm ⁻¹	1550 cm ⁻¹	1080 cm ⁻¹
2.	Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde titanium (III) chloride, [Ti(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Dark Yellow	178	32.40 (32.35)	2.92 (2.90)	6.30 (6.27)	1.73 (10.71)	65	-	1595 cm ⁻¹ (1:1)	1565 cm ⁻¹ electrolyte)	1080 cm ⁻¹
3.	Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde manganese(III) chloride, [Mn(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Brown	182	31.90 (31.00)	2.88 (2.84)	6.20 (6.13)	4.87 (11.67)	68	-	1600 cm ⁻¹ (1:1)	1563 cm ⁻¹ electrolyte)	1080 cm ⁻¹
4.	Tri aqua-2-furoic acid hydrazide-5-chloride, [Co(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Reddish Brown	186	31.62 (30.84)	2.85 (2.71)	6.15 (5.96)	12.93 (12.86)	70	-	1595 cm ⁻¹ (1:1)	1561 cm ⁻¹ electrolyte)	1080 cm ⁻¹
5.	Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde iron (III) chloride, [Fe(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Dark Brown	188	31.84 (30.92)	2.87 (2.84)	6.19 (6.09)	5.89 (12.29)	75	-	1595 cm ⁻¹ (1:1 electrolyte)	1564 cm ⁻¹	1080 cm ⁻¹
6.	Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde ruthenium (III) chloride, [Ru(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Green	208	28.94 (27.34)	2.61 (2.55)	5.62 (5.57)	1.88 (20.21)	66	-	1600 cm ⁻¹ (1:1 electrolyte)	1565 cm ⁻¹	1080 cm ⁻¹
7.	Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde rhodium (III) chloride, [Rh(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Dull White	195	28.83 (27.87)	2.60 (2.55)	5.61 (5.50)	0 (19.68)	69	-	1600 cm ⁻¹ (1:1 electrolyte)	1563 cm ⁻¹	1080 cm ⁻¹
8.	[Tri aqua-2-furoic acid hydrazide-5-bromo salicylaldehyde vanadium (III) chloride, [V(C ₁₂ H ₇ N ₂ O ₃ Br).3H ₂ O]Cl	Yellow	180	32.19 (31.04)	2.90 (2.71)	6.26 (5.99)	2.87 (10.94)	72	-	1595 cm ⁻¹ (1:1 electrolyte)	1562 cm ⁻¹	1080 cm ⁻¹

(The observed value given in bracket)

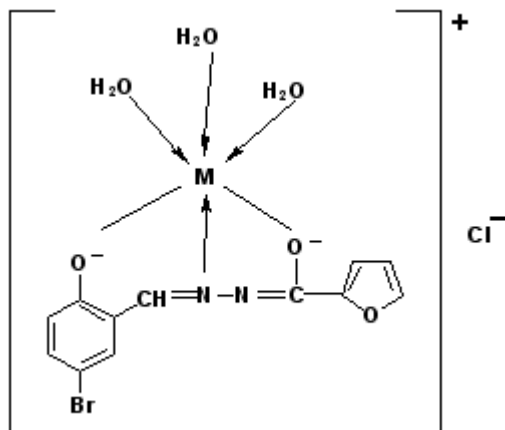
conjugation with the $-N=C$ group⁵. A strong band in the Schiff base at 1620 cm^{-1} is assigned to the $(C=N)$ which undergoes a negative shift by $20\text{-}25\text{ cm}^{-1}$ in the complexes indicating nitrogen coordination of the Schiff base⁶. The $(C-OH)$ (phenolic) mode of the Schiff base (1550 cm^{-1}) undergoes a positive shift by $10\text{-}15\text{ cm}^{-1}$ suggesting the coordination of the phenolic C-O group¹¹.

A new band at $1220\text{-}1260\text{ cm}^{-1}$ in the complexes is assigned to the $\frac{1}{2}(C-O)$ (phenolic) mode⁷. The $(C-O-C)$ mode of furan moiety occurs in the free ligand at 1080 cm^{-1} , this band remains unaffected in the complexes indicating the non-involvement of the oxygen atom of furan moiety in coordination. Thus, the IR data indicates that the Schiff base behaves as a tridentate ligand coordinating through ONO donor system.

The IR spectra of the complexes show non-ligand bands in the region of $3460\text{-}3510\text{ cm}^{-1}$ due to $\frac{1}{2}(O-H)$ and $835\text{-}855\text{ cm}^{-1}$ assignable to rocking mode of coordinated water molecules. TGA also supported the coordinated nature of the water molecules. The thermogram shows the % wt loss corresponding to the loss of three water molecules at $190\text{ }^{\circ}\text{C}$ ⁸.

Electronic spectra

The μ_{eff} of Ru(III) was found to be 1.88 B.M. as expected for an octahedral complex with t_{2g}^5 configuration. Its electronic spectrum in chloroform displayed bands at 13650 , 17600 and 22500 cm^{-1} , which may be assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$, ${}^2T_{1g} \rightarrow {}^4T_{2g}$, ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$ respectively¹³. The electronic



spectrum of diamagnetic Rh(III) in chloroform exhibited band at 17500 , 20100 , 24800 cm^{-1} as expected for assignable to ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. The last two bands have quite high value of ϵ , indicating their charge transfer nature. The first one may be assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition¹⁴.

The electronic spectrum of Ti(III) complex shows a single broad band at 19360 cm^{-1} due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition O_h symmetry¹¹. The value of magnetic moment of this complex is 1.73 B.M. which is in the expected range for d^1 system like Ti(III) and shows paramagnetic character of the complex. It also shows that Ti(III) has not been oxidized to Ti(IV) during or after complexation although it is very sensitive to oxidation.

The Mn(III) complex shows a magnetic moment of 4.87 B.M., corresponding to the presence of four unpaired electrons and high spin state of the complex. This value also suggests the absence of any kind of exchange interaction¹⁶. The electronic spectrum of complex shows an intense and sharp band at 22500 cm^{-1} which may be assigned to $Mn(d\pi) \rightarrow \pi$ (Azomethine) and a shoulder at 18540 cm^{-1} which may be assigned to ${}^5E_g \rightarrow {}^5T_{2g}$ transition characteristics of octahedral geometry¹⁶.

The study of magnetic properties of the Co(III) complex indicated diamagnetic nature, as expected for a low spin d^6 ion. The electronic spectrum of the chelate displays bands at 15344 , 21236 and 23540 cm^{-1} assignable to ${}^1A_{1g} \rightarrow {}^3A_{2g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transitions respectively. These are characteristic of low spin octahedral complexes of Co(III)¹³.

The observed value of effective magnetic moment of the V(III) complex is 2.87 B.M., as expected for d^2 system. The electronic spectrum of the complex exhibits a band at 16200 cm^{-1} with a shoulder at 20610 cm^{-1} . The low energy band may be assigned to ${}^2A_{1g} \rightarrow {}^3T_{2g}$ and the high energy band to ${}^2A_{1g} \rightarrow {}^3T_{2g}$. These are characteristic of octahedral geometry¹⁸.

The magnetic moment of Fe(III) complex is 5.89 B.M. corresponding to the presence of five unpaired electrons and high spin state of Fe(III) in

this complex. The electronic spectrum of this complex shows three bands at 12810, 19576 and 25500 cm^{-1} due to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4E_g$ (G) transitions respectively in an octahedral symmetry¹⁸.

CONCLUSION

Based on the studies performed and

discussed above, an octahedral geometry has been proposed for all the synthesized complexes.

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