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SYNTHESIS AND CHARACTERIZATION OF CHROMIUM (III) COMPLEXES OF N, O AND S DONOR LIGANDS

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ABSTRACT

New chromium (III) complexes of N, O and S donor ligands such as furfuralidene semicarbazone (LH), furfuralidene thiosemicarbazone (L^1H), vanilidene thiosemicarbazone (L^2H_2), vanilidene aniline (L^3H), vanilidene fluoroaniline (L^4H) and bis-vanilidene hydrazone (L^5H_2) were synthesized. The resulting chromium (III) complexes were characterized on the basis of elemental analysis, conductance measurements, molecular weights determination, IR, ^1H NMR and UV-Vis. spectral studies. The ligands act as a monofunctional bidentate, monofunctional tridentate and bifunctional tridentate donors and coordinate through furfural oxygen, phenolic oxygen, azomethine nitrogen, enolic oxygen and thioenolic sulphur atoms. The antibacterial activity of the ligands and their complexes has been screened against *S. aureus* and *E. coli*. The spectral data suggested a six coordinate geometry around the chromium (III) metal ion.

Key words: Chromium (III) complexes, Schiff base ligands, Spectral, Biological.

INTRODUCTION

Compounds containing an azomethine group (-CH = N-) are known as Schiff bases. Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in the different spheres[1-3]. Schiff bases are generally bi- or tri-dentate ligands capable of forming very stable complexes with transition metals. Semicarbazones and thiosemicarbazones constitute one of the most important classes of sulphur, oxygen and nitrogen donor ligands[4]. The formations of a variety of metal complexes from these ligands speak for their spectacular progress in coordination and bioinorganic chemistry[4]. Some other metal complexes of semicarbazone and thiosemicarbazone ligands particularly sulphur containing, are drawing enormous attention mainly due to their practical utility. They are active against cancer[5], viruses[6], ulcer[7] and certain kinds of tumours. Chromium has d^5s^1 outer electronic configuration and +3 oxidation state is the most important and the most stable state of it. This state also forms a large number of complexes. Chromium (III)

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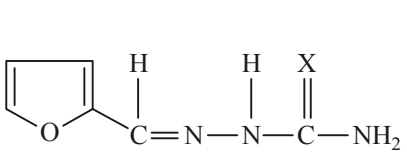
complexes are of great importance due to their biological, pharmacological, clinical and analytical applications[8]. Chromium (III) complexes of nitrogen donor ligands are of much importance[9,10]. Chromium has been considered to be an essential trace element in the experimental animals and probably in man, where chromium is present in the trivalent state[11,12]. Of interest is the fact that Cr (III) biologically acts as a co-factor in the initiation of insulin –S and tissue insulin receptor –SH, facilitating the initial insulin- tissue interaction. The hypothetical Cr (III) complexes occurring in brewer's yeast and other foods termed as "glucose tolerance factor", were found to possess outstanding biological activity[13]. Although chromium deficiency is difficult to achieve, it is excreted after insulin challenge in the form of oligopeptide. To understand the characteristic nature and applications of the biologically active metal complexes of sulphur / oxygen and nitrogen donor ligands, the present course of study was initiated with preparation, characterization and biological screening of the complexes of chromium with biologically relevant ligands.We report herein the synthesis of some Schiff base complexes and their characterization by means of spectral studies. Octahedral structure has been proposed for the complexes.

EXPERIMENTAL

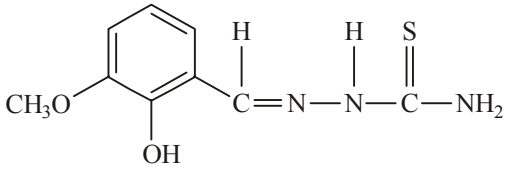
The $CrCl_3.6H_2O$ was purchased from Thomas Baker. All the reagents were dried and distilled before use. o- Vanillin was purchased from SISCO Chem., Bombay, India. Aniline, fluoroaniline, hydrazine hydrate, semicarbazide and thiosemicarbazide were used as such.

Synthesis of the ligands

The ligands were synthesized by the condensation of furfuraldehyde with semicarbazide hydrochloride (LH), or thiosemicarbazide (L^1H) and vanillin with thiosemicarbazide (L^2H_2), aniline (L^3H) or fluoroaniline (L^4H) in 1 : 1 molar ratio and by reacting vanillin with hydrazine hydrate (L^5H_2) in 2 : 1 molar ratio in ethanol followed by refluxing the reaction mixture on a water bath for 2 to 3 hours. The precipitates thereby obtained were separated and washed with ethanol and dried in vacuo in desiccator over anhydrous calcium chloride at the room temperature (Fig. 1).



LH [X = O]
L^1H [X = S]



L^2H_2

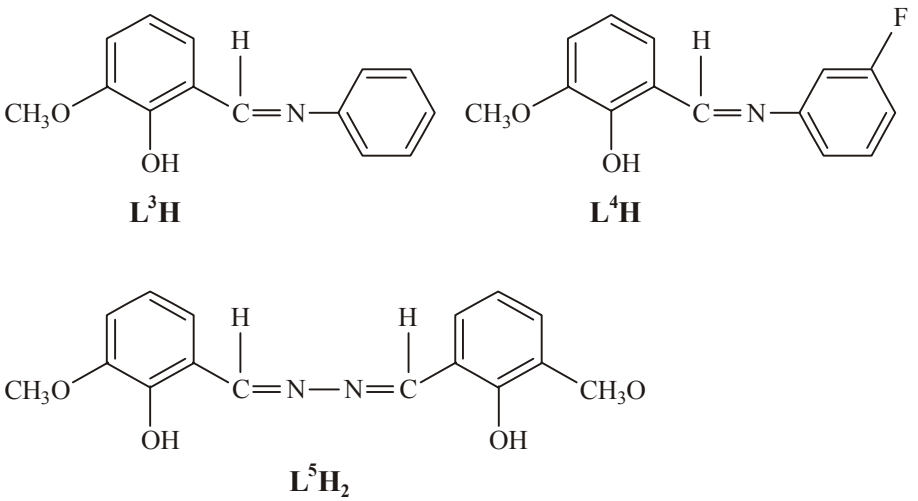


Fig. 1: Structures of ligands

Synthesis of the complexes

To an ethanolic solution (25 mL) of the ligand (1 mol), metal chloride (1 mol) in ethanol was added. The reaction mixture was refluxed on the a water bath for 3 to 4 hours. The precipitates of the resulting metal complexes were filtered, washed with ethanol and dried in vacuo in a desiccator over anhydrous calcium chloride at the room temperature.

Physical measurements and analytical methods

The carbon, hydrogen and nitrogen analyses were performed by the Elemental Vario EL (III) Carlo Erba 1108. The IR spectra of the ligands and their complexes were scanned as KBr pellets on a Perkin –Elmer 575 spectrophotometer. The ^{1}H NMR spectra of the ligands were recorded on Bruker -300 FT NMR spectrometer in DMSO-d_6 using TMS as an internal standard. The molar conductances of the complexes were determined by a conductivity meter with a dip type cell and platinized electrode. UV - Vis. spectra of the complexes were recorded on Thermospectronic 200 -1100 nm. Melting points were measured in open capillaries and are uncorrected. Molecular weights of the complexes were determined by Rast method using camphor as a solvent. Metal contents of the complexes were determined by the atomic absorption technique. Chloride was determined by the standard procedure reported in the literature[14]. The antibacterial activity was evaluated by agar disc diffusion method.

RESULTS AND DISCUSSION

The reactions of $CrCl_3.6H_2O$ with the ligands have been carried out in unimolar ratio in ethanol. The successive replacement of chloride resulted in the formation of products as shown below (**Scheme 1**).

The overall reactions of 1 : 1 complexes are as follows:

$$CrCl_3.6H_2O + LH \rightarrow [Cr\ (L)\ (H_2O)Cl_2] + 5\ H_2O + HCl \quad ...(1)$$

$$CrCl_3.6H_2O + L^1H \rightarrow [Cr\ (L^1)\ (H_2O)Cl_2] + 5\ H_2O + HCl \quad ...(2)$$

$$CrCl_3.6H_2O + L^2H_2 \rightarrow [Cr\ (L^2)\ (H_2O)_2Cl] + 4\ H_2O + 2\ HCl \quad ...(3)$$

$$CrCl_3.6H_2O + L^3H \rightarrow [Cr\ (L^3)\ (H_2O)_2Cl_2] + 4\ H_2O + HCl \quad ...(4)$$

$$CrCl_3.6H_2O + L^4H \rightarrow [Cr\ (L^4)\ (H_2O)_2Cl_2] + 4\ H_2O + HCl \quad ...(5)$$

$$CrCl_3.6H_2O + L^5H_2 \rightarrow [Cr\ (L^5)\ (H_2O)_2Cl] + 4\ H_2O + 2\ HCl \quad ...(6)$$

Scheme 1

Where LH, L^1H, L^2H_2, L^3H, L^4H and L^5H_2 represents the ligand molecules.

The physical properties and analytical data of the ligands and their metal complexes are enlisted in Table 1.

Table 1: Synthetic and analytical data of the ligands and their chromium complexes

Compounds	Mol. Wt. Found/(Calc.)	Colour	M.P.	% Found / (Calc.)				
				C	H	N	M	Cl
$LH(C_6H_7N_3O_2)$	164.01 (153)	Greyish	173	47.00 (47.06)	4.51 (4.57)	27.63 (27.45)	-	-
$L^1H(C_6H_7N_3OS)$	172.32 (169)	Dark Grey	152	42.69 (42.60)	4.03 (4.14)	24.71 (24.85)	-	-

Cont…

Compounds	Mol. Wt. Found/(Calc.)	Colour	M.P.	% Found / (Calc.)				
				C	H	N	M	Cl
$L^2H_2(C_9H_{11}N_3O_2S)$	230.09 (225)	Dull White	137	48.14 (48.00)	4.53 (4.89)	18.96 (18.67)	-	-
L^3H $(C_{14}H_{13}NO_2)$	219 (227)	White	178	74.00 (74.01)	4.99 (5.73)	6.01 (6.17)	-	-
L^4H $(C_{14}H_{12}NO_2F)$	252.33 (245)	Light Yellow	165	68.44 (68.57)	4.33 (4.89)	5.79 (5.71)	-	-
$L^5H_2(C_{16}H_{16}N_2O_4)$	291.08 (300)	Orange	145	63.86 (64.00)	5.02 (5.33)	9.14 (9.33)	-	-
$[Cr(L)(H_2O)Cl_2]$	288.15 (293)	Green	160	24.47 (24.57)	2.63 (2.73)	14.30 (14.33)	17.35 (17.75)	24.13 (24.23)
$[Cr(L^1)(H_2O)Cl_2]$	304 (309)	Dark Green	110	23.00 (23.00)	3.06 (3.23)	13.51 (13.59)	16.63 (16.83)	22.91 (22.98)
$[Cr(L^2)(H_2O)_2Cl]$	341 (346.5)	Dark Brown	167	31.11 (31.17)	4.01 (3.75)	12.10 (12.12)	15.00 (15.01)	10.19 (10.24)
$[Cr(L^3)(H_2O)_2Cl_2]$	375.34 (385)	Green	172	43.64 (43.64)	4.40 (4.15)	3.32 (3.64)	12.48 (13.51)	18.40 (18.44)
$[Cr(L^4)(H_2O)_2Cl_2]$	398.11 (403)	Dark Green	110	(43.64) 41.68	3.70 (3.72)	3.40 (3.47)	12.81 (12.90)	17.60 (17.62)
$[Cr(L^5)(H_2O)_2Cl]$	406.19 (421.5)	Yellow	186	(41.69) 45.53	4.26 (4.27)	6.87 (6.64)	12.30 (12.34)	8.43 (8.42)

The analytical data (Table 1) indicate that the metal – ligand stoichiometry is 1 : 1 in all the complexes. All the complexes are coloured solids, insoluble in water but soluble in DMF and DMSO. The molar conductivity values for the complexes in dimethyl sulfoxide have been found in the range 5 - 17Ω^{-1} cm^2 mol^{-1} indicating their non – electrolytic nature[15].

IR Spectral studies

The IR spectra of the ligands showed a band in the range 1647 – 1607 cm^{-1}, which is due to ν C=N. This band shifts to lower frequency 1605 – 1590 cm^{-1} in all the chromium

complexes, indicating that bonding is taking place through the azomethine nitrogen[16,17]. The characteristic phenolic ν (O-H) mode due to presence of a hydroxyl group at ortho position in the ligands (L^2H_2), (L^3H), (L^4H) and (L^5H_2) was observed at 3293-3180 cm^{-1} .A band at 1230 – 1274 cm^{-1} due to ν (C-O)[17] phenolic was also observed in the ligands (L^2H_2), (L^3H), (L^4H) and (L^5H_2). The disappearance of phenolic ν (O-H) bands in all the complexes under study suggests the coordination by the phenolic oxygen (after deprotonation) to the chromium (III) metal ion[18]. This is further supported by the shifting of ν (C-O) phenolic to lower wave numbers in L^2, L^3, L^4 and L^5 chromium (III) metal complexes. In the ligands, strong bands due to ν C=O and ν C=S appeared at 1666 cm^{-1} (LH) and 1060 cm^{-1} (L^1H) as well as 1045 cm^{-1} (L^2H_2), respectively. These bands disappeared in the complexes, suggesting enolization and thioenolization of the ligands and their chelation through enolic oxygen and thioenolic sulphur, respectively[19,20]. A broad band appeared in all the complexes in the range 3400 – 3300 cm^{-1}, indicating the presence of water molecules[21]. Infrared spectra of the ligands (LH, L^1H and L^2H_2) showed bands at 3174 - 3180 cm^{-1} due to ν NH vibrations. In the spectra of the metal complexes these bands disappear, indicating deprotonation followed by coordination[22]. The complexes also showed medium intensity bands in the region 586 – 548 cm^{-1} and 480-468 cm^{-1}, which can be attributed to ν Cr-N and ν Cr-O band, respectively.[23]

Electronic spectral data of chromium (III) complexes

The electronic spectra of all the chromium (III) complexes were recorded in DMSO. These spectra are quite similar to one another and may be interpreted on the basis of an octahedral environment around chromium (III) metal ion in these complexes. The complexes showed three bands at 16806-18518 cm^{-1}, 22831-23529 cm^{-1} and 31250-32573 cm^{-1} which have been assigned to $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_2), and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively in the order of increasing energy[24, 25].

^{1}H NMR spectra

The proton magnetic resonance spectra of L^3 H and L^4 H ligands have been recorded in DMSO- d_6. The chemical shift values (δ) for different protons are given in Table 2. The signals observed at δ 9.76 and 13.09 ppm are due to phenolic protons in L^3H and L^4H ligands, recpectively[26]. A singlet is observed at δ 3.85 and 3.83 ppm, which may be assigned to the presence of methoxy protons in these ligands. A complex multiplet observed at δ 6.96 ppm is due to the aromatic protons.

Table 2: ^{1}H NMR Spectral data of L^3H and L^4H Ligands

Ligands	Chemical Shift (δppm)	Peak	No. of protons	Group assigned
$C_{14}H_{13}NO_2$	3.85	Singlet	3	OCH_3
	6.96	Complex multiplet	1	Aromatic ring
	9.76	Singlet	1	OH
$C_{14}H_{12}NO_2F$	3.83	Singlet	3	OCH_3
	6.96	Complex multiplet	1	Aromatic ring
	13.09	Singlet	1	OH

Thus, on the basis of the above studies, the expected structures of the complexes may be represented as –

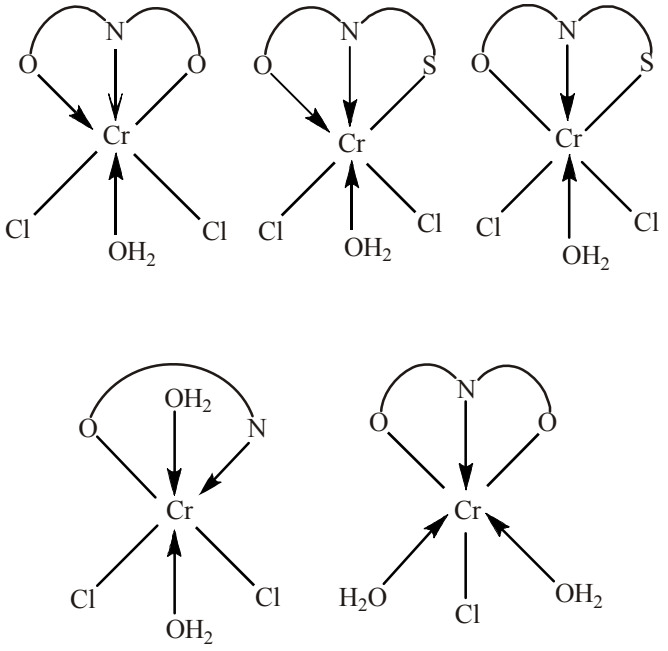


Fig. 2: The parts involving O, N and S atoms in above structures represent the donor systems of the ligands

Antibacterial activity

The antibacterial activity of the ligands and their metal complexes has been studied by paper plate method[27]. All the glasswares used were sterilized in an autoclave before its use. The ligands and their metal complexes were tested against bacterial species *S. aureus* and *E. coli*. In this technique, sterilized hot nutrient [composition : peptone (5 g), beef extract (5 g), NaCl (5 g), and agar-agar (20 g) and distilled water 1000 mL] and 5 mm. diameter paper discs of Whatman filter paper No. 1 were used. The agar medium was poured into the petri plates. When it is solified, 5 mL of warm seeded agar was applied. The seeded agar was prepared by cooling the molten agar to 40°C and then 10 mL of bacterial suspension was added. The compound was dissolved in DMSO to give 500 and 1000 ppm concentrations. Paper discs were soaked in these solutions of varied concentrations. The discs were dried and placed on the medium previously seeded with organisms in the petri plates at suitable distance. The petri plates were stored in an incubator at 28 ± 2°C for 24 hours. Growth inhibition zone diameters were measured in mm. The ligands show less activity than that shown by the complexes. The results are summarized in Table 3.

Table 3: Antibacterial screening data for the ligands and their complexes

Compounds	Antibacterial activity			
	Diameter (mm) of inhibition zone after 24 h (conc. in ppm)			
	E. coli		*S. aureus*	
	500	1000	500	1000
$LH(C_6H_7N_3O_2)$	11	11.3	12	13
$L^1H(C_6H_7N_3OS)$	8	9	10	11
$L^2H_2(C_9H_{11}N_3O_2S)$	9	9.7	10	10.9
$L^3H\ (C_{14}H_{13}NO_2)$	8	8.7	9	9
$L^4H\ (C_{14}H_{12}NO_2F)$	8	8.7	8.6	9.2
$L^5H_2(C_{16}H_{16}N_2O_4)$	10	12	11	12
$[Cr(L)(H_2O)Cl_2]$	14	14.5	15	15
$[Cr(L^1)(H_2O)Cl_2]$	15	15	16	16

Cont…

Compounds	Antibacterial activity			
	Diameter (mm) of inhibition zone after 24 h (conc. in ppm)			
	E. coli		*S. aureus*	
	500	**1000**	**500**	**1000**
$[Cr(L^2)(H_2O)_2Cl]$	15	15.7	15	15.8
$[Cr(L^3)(H_2O)_2Cl_2]$	11.2	11	16	17
$[Cr(L^4)(H_2O)_2Cl_2]$	9	9	10	11
$[Cr(L^5)(H_2O)_2Cl]$	11	11.4	16	16
Norfloxacin (standard)	18	19.2	20	22

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