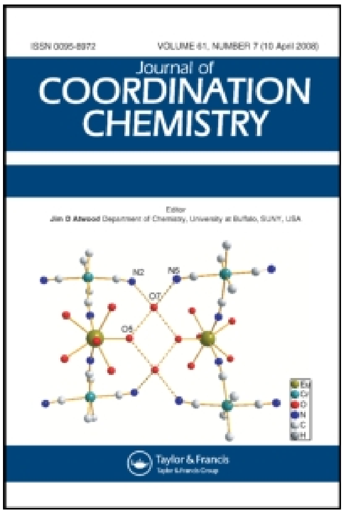

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Reactions of 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine with chromium(III) salts leading to newer synthesis of chromium(III) complexes

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Reactions of 2-(L-carboxyl-2-hydroxyphenyl)thiazolidine with different chromium(III) salts [$CrCl_3 \cdot 6H_2O$, $K_3[Cr(SCN)_6]$, $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$, $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ and $[Cr(CH_3COO)_2H_2O]_2$] under varied reaction conditions afforded many new mixed-ligand chromium(III) complexes. The ligand is a tridentate dibasic NSO donor except for complexes **1** and **4** where two moles of the ligand are present for each molecule of complex, one functioning as a dibasic tridentate (NSO) and the other as a monobasic bidentate (NS) (phenolic OH and carboxylic COOH groups remaining uncoordinated). The complexes have been characterized by elemental analyses, magnetic susceptibilities, molar conductances, molecular weights and spectroscopic (IR, Uv-vis) data. The ligand field parameters and NSH Hamiltonian parameters suggest tetragonal geometries of the complexes.

Keywords: 3-Formylsalicylic acid; Schiff base; Thiazolidine; Chromium(III) compounds; NSH parameters

1. Introduction

The toxicity of chromium complexes is well defined. Chromium compounds are carcinogens and are corrosive to human tissue; insoluble chromium compounds are retained in the lungs and are implicated in the occurrence of lung cancer. Cancer in the respiratory system and antrum are caused by chromium [1]. The toxicity of metals at the molecular level are seen because of their ability to bind to peptide residues of proteins, notably histidine and cysteine residues. Therefore, complexes in which the metal is coordinated to an L-amino acid (e.g. L-histidine) may be excellent models for the therapeutic action of D-penicillamine and its analogues. Hypothetical chromium(III) complexes occurring in brewers' yeast and other foods, termed "glucose tolerance factor" were found to be of outstanding biological activity [2]. Chromium(III) complexes of NS and NSO donor ligands are involved in the above processes.

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Metal complexes of ligands derived from 3-formylsalicylic acid have been extensively studied by Dey *et al.* [3–7] and others [8–12]. Recently Dey *et al.* [4, 7] synthesized two new ligands 2-(1-carboxyl-2-hydroxyphenyl)benzothiazoline (abbreviated to H_2chpbzn) and 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (abbreviated to H_2chptz) by the condensation of 3-formylsalicylic acid with 2-aminobenzethiol and 2-aminoethanethiol, respectively, and studied their reactions with transition and non-transition metal salts leading to many new metal complexes. Organometallic derivatives of these ligands have also been studied [3–8, 13]. The above ligands H_2chpbzn and H_2chptz, in course of reactions rearranged to Schiff-base forms and function as NSO donor ligands. In continuation of that study we have carried out reactions of 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine with different chromium(III) salts/complexes, viz., $CrCl_3 \cdot 6H_2O$, $K_3[Cr(SCN)_6]$, $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$, $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ and $[Cr(CH_3COO)_2H_2O]_2$ under varied reaction conditions and isolated many new mixed-ligand complexes of chromium(III) and characterized them. It is pertinent to mention here that in the present chromium(III) complexes, NSO and NS donor ligands are involved in complex formation, relevant to biological activity of chromium complexes.

2. Experimental

2.1. *Materials and instruments*

All solvents were purified and dried according to standard procedures [14] before use. Elemental analyses of the complexes were carried out on Elementar Vario EL III, Carlo Erba 1108 elemental analyzers at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India. Nitrogen was also analyzed in our laboratory by usual methods (By Duma's method). Infrared spectra were recorded in KBr, Nujol or hexachlorobutadiene (several media were used for some compounds) on Perkin-Elmer 1330 and L120-000A spectrophotometers. The electronic spectra were recorded on a Hitachi 200-20 and Simadzu UV-2401PC spectrophotometers. Conductance measurements were made with a conductivity bridge (Elico Pvt. Ltd., Model CM 80). The magnetic susceptibility was determined by the Guoy method at room temperature. Molecular weights were determined by Rast's method [15, 16].

2.2. *Preparation of the ligand*

The thiazolidine ligand, H_2chptz, was prepared by our previously published method [7].

2.3. *Preparation of the chromium(III) complexes*

2.3.1. $[(H_2mcsalim)(Hmcsalim)(H_2O)Cr] \cdot 4H_2O$ (1). The ligand H_2chptz (0.56 g, 0.0025 mole) was dissolved in ethanol (30 mL) to which a solution of $CrCl_3 \cdot 6H_2O$ (0.665 g, 0.0025 mole) in the same solvent (30 mL) was added with stirring followed by addition of a stoichiometric amount of CH_3COONa (0.205 g, 0.0025 mole) and the mixture was refluxed for 3 h. The light brown solution thus obtained gave a light yellow compound on standing, which was filtered, washed with cold ethanol and dried *in vacuo*. Yield, 0.72 g (48%).

The reaction of H_2chptz and Cr(gly)$_3$ (where gly is glycinateion) in equimolecular ratio in ethanol yielded the same compound.

2.3.2. NH_4[(Hmcsalim)$_2$Cr] • 4H_2O (2). Similarly, a mixture of H_2chptz (1.12 g, 0.005 mole) and $CrCl_3 \cdot 6H_2O$ (0.665 g, 0.0025 mole) in ethanol (70 mL) was heated under reflux for 30 min; then NH_4OH (15% alcoholic solution) was added to raise the pH to 9. The mixture was heated for another 30 min and filtered while hot. The brown solution was concentrated and kept in a refrigerator to get light yellow precipitate, which was filtered off, washed with ethanol and dried *in vacuo*. Yield, 1.13 g (75%).

2.3.3. NH_4[(Hmcsalim)(SCN)$_2$(H_2O)Cr] • 2H_2O (3). A hot ethanolic solution (30 mL) of H_2chptz (0.56 g, 0.0025 mole) was added to a hot ethanolic solution (30 mL) of $K_3[Cr(SCN)_6]$ (1.29 g, 0.0025 mole) and the mixture (pH = 5) was heated under reflux for 3 h and filtered while hot. The volume of the filtrate was reduced to half of its original volume and the pH of the solution was raised to about 9 by dropwise addition of 15% aqueous ammonia. It was then heated on a water bath for further 15 min to remove excess ammonia. On cooling, a brown solid precipitated, was collected by filtration, washed with cold ethanol and dried *in vacuo*. Yield, 0.63 g (55%).

2.3.4. [(H_2mcsalim)(Hmcsalim)(H_2O)Cr] (4). The above reaction, when carried out in 2 : 1 molar ratio (ligand : metal) at pH = 5 in ethanol, a brown precipitate separated while under reflux. The compound was filtered off, washed with ethanol and dried *in vacuo*. Yield, 0.87 g (68%).

2.3.5. NH_4[(Hmcsalim)$_2$Cr]2H_2O (5). When hot ethanolic solution (50 mL) of H_2chptz (0.56 g, 0.0025 mole) was added to a hot ethanolic solution (50 mL) of $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$ (0.885 g, 0.0025 mole) a brown solution (pH = 5) was obtained. The solution was heated under reflux for 2 h and filtered while hot. The pH of the filtrate was raised to about 9 by adding 15% ethanolic ammonia solution. This was heated for 20 min on a water bath and the volume was reduced to half of its original volume, which on cooling gave a greenish yellow compound, which was filtered off, washed with ethanol and dried *in vacuo*. Yield, 0.69 g (50%).

2.3.6. [(Hmcsalim)(NH_3)$_2$(H_2O)Cr]SCN (6). The above reaction, when carried out in 2 : 1 molar ratio (ligand : metal) at pH = 5 in ethanol, a yellow brown precipitate was separated out while under reflux. The compound was filtered off, washed with ethanol and dried *in vacuo*. Yield, 0.67 g (70%).

2.3.7. [(Hmcsalim)(Cl)(H_2O)$_2$Cr] (7). An ethanolic solution (30 mL) of H_2chptz (0.56 g, 0.0025 mole) was added to a hot ethanolic solution (containing few drops of water) (30 mL) of $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ (1.43 g, 0.0025 mole). The pH of the mixture was raised to 8 by adding 15% ethanolic ammonia solution followed by reflux for 3 h.

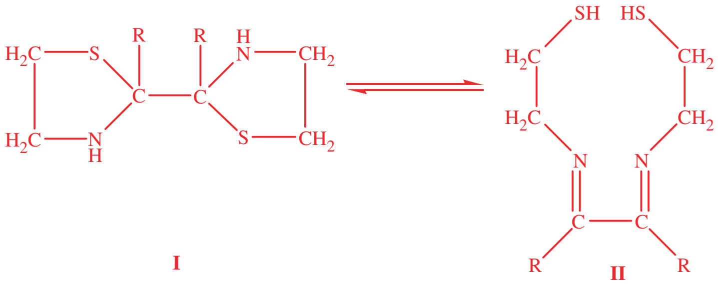


Figure 1. Tautomerism between *bis*(thiazolidine) and Schiff base.

It was filtered while hot and the filtrate on concentration and cooling gave a light yellow compound. Yield, 0.52 g (60%).

2.3.8. [(Hmcsalim)(CH_3COO)(H_2O)$_2$Cr] (8). Freshly prepared [Cr(CH_3COO)$_2$$H_2O$]$_2$ [17] (0.94 g, 0.0025 mole) was dissolved in ethanol (60 mL) and was added to a solution of H_2chptz (0.56 g, 0.0025 mole) in ethanol and the mixture was heated under reflux for 3 h and filtered while hot. This filtrate, on concentration and cooling, gave this brown compound. Yield, 0.56 g (60%).

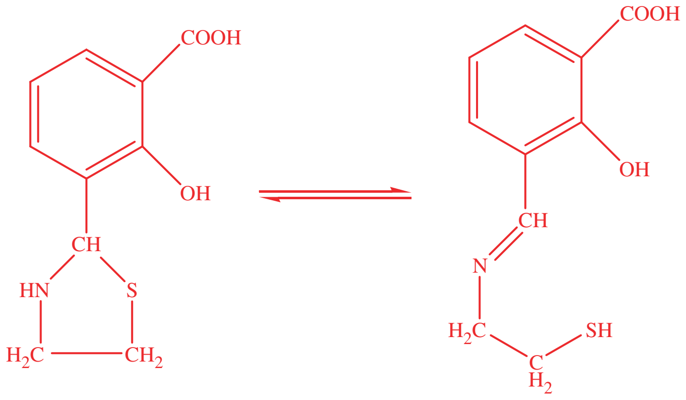
2.3.9. [(Hmcsalim)(Py)(Cl)(H_2O)Cr] (9). The ligand H_2chptz (0.56 g, 0.0025 mole) and $CrCl_3 \cdot 6H_2O$ (0.665 g, 0.0025 mole) was taken in freshly distilled boiling pyridine (60 mL) followed by addition of Zn-dust (excess). The mixture was refluxed (on a sand bath) for 3 h and filtered. The filtrate was concentrated to half of its original volume and few drops of distilled water was added and stirred thoroughly, whereby a yellow brown precipitate separated, was filtered, washed with ethanol and dried *in vacuo*. Yield, 0.61 g (60%).

3. Results and discussion

3.1. *Syntheses*

The condensation of 2-aminobenzethiol and 2-aminoethanethiol with aldehyde normally yields benzothiazoline and thiazolidine, respectively [13]; some oxidized products can also be isolated in both the cases. The reaction of α-diketones and 2-aminoethanethiol results in *bis*(thiazolidine) (**I**) as the main product, along with a small amount of the tautomeric Schiff base (**II**), which may remain in equilibrium in solution (figure 1). However the presence of nickel(II) results in formation of the nickel(II) complex of the corresponding Schiff base (**II**) in good yield [13].

In the present investigation, we observed that reaction of 3-formylsalicylic acid with 2-aminoethanethiol under dry nitrogen atmosphere and mild conditions afforded yellow 2-(1-carboxyl-2-hydroxyphenyl)thiazolidine (abbreviated to H_2chptz) in good yield. However, in solution, this remains in equilibrium with a small amount of the corresponding Schiff base, 3-carboxysalicylidenethioethanolimine (abbreviated to H_3mcsalim) (**III**) (figure 2) [7].



(H_2chptz)
(a)

(H_3mcsalim)
(b)

III

Figure 2. Tautomerism between thiazolidine (H_2chptz) and the Schiff base (H_3mcsalim).

However in the solid state, the thiazolidine structure has been suggested from the infrared spectroscopic data. The reaction of the thiazolidine, H_2chptz, with the stoichiometric amount of chromium(III) salts under varied reaction conditions afforded chromium(III) complexes, in which the Schiff base is a dibasic tridentate NSO donor except in complexes **1** and **4**. In these two complexes the Schiff base simultaneously functions as a dibasic tridentate NSO donor and monobasic bidentate NS donor. All complexes can be isolated by *in situ* reaction of the metal salt with the ligand components in suitable solvent. The complexes isolated are all stable at room temperature and have been characterized by elemental analyses, molecular weights, molar conductance values, magnetic moments and spectroscopic (UV-Vis, IR and ^{1}H NMR) data. Some of the characterization data are shown in table 1. Unfortunately single crystals could not be grown in spite of our best efforts. However, calculated values of ligand field parameters and NSH Hamiltonian parameters help to propose plausible geometry of the isolated chromium(III) complexes.

3.2. *Molar conductance values*

The molar conductance values of 10^{-3} M solutions (in DMSO) of **1**, **4**, **7**, **8** and **9** are recorded in table 1, and the values indicate non-electrolytic nature of the complexes. The Λ_M values for **2**, **3** and **6** (table 1) indicate 1 : 1 electrolytic nature [18]. Molecular weights also support the formulations of the complexes.

3.3. *Infrared and ^{1}H NMR spectra*

The IR spectrum of the thiazolidine H_2chptz show a number of important vibrations at 1705(s), 3450(br), and 3100(br) cm^{-1} assignable to ν(COOH), ν(OH) and ν(NH), respectively. The complete eliminations of ν(CHO) at 1660 cm^{-1} (observed in 3-formylsalicylic acid) supports condensation. Further, the absence of bands around

Table 1. Some characterization data of the chromium(III) complexes.

Compound	Colour	M.p. (°C)	Mol. wt found (Calcd)	Analyses found (Calcd) %					μ_{eff}[a] B.M.	Λ_M[b] Ω^{-1} $cm^2 mol^{-1}$
				C	H	N	Cl	Cr		
[(H_2mcsalim)(Hmcsalim)(H_2O)Cr] · $4H_2O$ (**1**)	Light-yellow	245–250(d)	612	40.60	4.29	4.66	–	8.53	3.84	12.40
$C_{20}H_{29}N_2S_2O_{11}Cr$			(589.59)	(40.74)	(4.96)	(4.75)		(8.82)		
NH_4[(H_2mcsalim)$_2$Cr] · $4H_2O$ (**2**)	Light-yellow	235–240(d)	568	39.99	4.87	9.67	–	8.65	3.80	50.20
$C_{20}H_{30}N_3S_2O_{10}Cr$			(602)	(39.86)	(4.98)	(9.30)		(8.63)		
NH_4[(Hmcsalim)$(SCN)_2$(H_2O)Cr] · $2H_2O$ (**3**)	Brown	305–308(d)	–	31.28	4.04	12.50	–	11.38	3.85	38.90
$C_{12}H_{19}N_4S_3O_6Cr$			(463.50)	(31.10)	(4.13)	(12.09)		(11.22)		
[(H_2mcsalim)(Hmcsalim)(H_2O)Cr] (**4**)	Dark-brown	232–233(d)	–	46.68	4.21	5.58	–	10.13	3.78	10.70
$C_{20}H_{21}N_2S_20_7Cr$			(517.74)	(46.44)	(4.06)	(5.41)		(10.05)		
NH_4[(H_2mcsalim)$_2$Cr] · $2H_2O$ (**5**)	Greenish-yellow	230–235(d)	–	43.21	4.38	7.51	–	9.59	3.81	42.80
$C_{20}H_{26}N_3S_2O_8Cr$			(552.57)	(43.47)	(4.74)	(7.60)		(9.41)		
[(Hmcsalim)$(NH_3)_2$(H_2O)Cr] SCN (**6**)	Yellow-brown	245–250(d)	–	34.42	4.16	14.22	–	13.41	3.86	40.90
$C_{11}H_{17}N_4S_2O_4Cr$			(385)	(34.28)	(4.41)	(14.54)		(13.50)		
[(Hmcsalim)(Cl)$(H_2O)_2$Cr] (**7**)	Light-yellow	240–243(d)	370	34.48	3.68	4.60	10.00	14.87	3.89	16.80
$C_{20}H_{29}N_2S_2O_{111}CrCl$			(346.73)	(34.64)	(3.78)	(4.04)	(10.22)	(14.99)		
[(Hmcsalim)(CH_3COO)$(H_2O)_2$Cr] (**8**)	Brown	240–245(d)	–	38.81	4.20	3.90	–	14.22	3.78	15.70
$C_{12}H_{16}NSO_7Cr$			(370.32)	(38.92)	(4.36)	(3.78)		(14.04)		
[(Hmcsalim)(Py)(Cl)(H_2O)Cr] (**9**)	Yellow-brown	245–250(d)	428	44.84	3.93	6.79	8.28	12.99	3.79	19.20
$C_{15}H_{16}N_2SO_4CrCl$			(407.82)	(44.18)	(3.95)	(6.87)	(8.69)	(12.75)		

[a] Solid state room temperature, [b] 10^{-3} M solution in DMSO at room temperature.

2500 and 1600 cm^{-1} assignable to ν(SH) and ν(C=N), respectively gives further support for the thiazolidine structure [**III**(**a**)].

Comparison of ^{1}H NMR spectra of the free ligand H_2chptz and diamagnetic zinc(II) complex [Zn(Hmcsalim)H_2O] [7] helps to determine the structure of the ligand and the chromium(III) complexes. The ^{1}H NMR data (in DMSO-d_6) showed the absence of δ(CHO) at around 9.65 ppm in the thiazolidine H_2chptz which was found in 3-formylsalicylic acid supporting the condensation. No azomethine proton signal δ(CH=N) could be detected either in its typical downfield position [7]. The broad δ(OH) signal at 8.8 ppm vanishes after addition of D_2O. The multiplets in the region δ 6.6 to 8.1 ppm may be assigned to the phenyl resonances. A broad signal at 4.6 ppm(2H) may be considered as thiazolic C–H and N–H with broadening from the quadruple moment of the nitrogen nucleus that induces moderately efficient spin relaxation [19]. The resonance peak for the –COOH proton could be detected around δ 12.8 ppm as a very broad and weak signal [4, 5, 19]. The ^{1}H NMR spectrum (in DMSO-d_6 of [Zn(Hmcsalim)H_2O] exhibits a sharp singlet at δ 8.5 ppm which corresponds to δ(HC=N) and indicates rearrangement of thiazolidine, to the Schiff base, H_3mcsalim, which ultimately forms complexes with the metal ions as dibasic tridentate NSO donor ligand. This conclusion may be extended for the present chromium(III) complexes (table 1), in most of them the Schiff base functions as a dibasic tridentate NSO donor ligand except in complexes **1** and **4** (see above and later discussion).

In the infrared spectra of the chromium(III) complexes the bands due to N–H and O–H vibrations are absent, suggesting bond formation of the ligand to chromium(III) through oxygen, nitrogen and sulphur. But in some cases, presence of H_2O and NH_3 makes the interpretation very difficult. In addition, a new band around 1610–1640 cm^{-1} is observed assignable to the ν(C=N) vibration. This also supports the fact that the thiazolidine ring in the presence of chromium(III) ion, rearranged to its Schiff-base form and is a dibasic tridentate NSO donor ligand in the complexes [20, 21] (table 1). The ν(C–S) mode of the ligand around 770–730 cm^{-1} is shifted to around 720–700 cm^{-1} in the metal complexes indicating a Cr–S linkage. This is further substantiated by the appearance of new bands in the regions 360–320 cm^{-1} in the metal complexes which are assignable to ν(Cr–S) [22, 23]. Other bands of ν(Cr–O) and ν(Cr–N) appear, respectively, at 560–540 and 500–480 cm^{-1} [4, 24] supporting O and N linkage to the chromium(III). The COOH group in all the complexes remained uncoordinated as evidenced by the appearance of infrared bands in the region 1710–1735 cm^{-1}. The very slight blue-shifting from the free ligand value (1705 cm^{-1}) is not clear and may be due to the combined effect of the rearrangement of the ligand structure, streospecific interaction with the coordinated metal ion and the presence of coordinated water. Some important infrared bands along with their tentative assignments are shown in table 2.

The presence of coordinated acetato group in **8** is confirmed by the appearance of the bands in the regions 1651 and 1360 cm^{-1} [25]. Furthermore, the appearance of a broad band around 3540–3330 cm^{-1} in the complexes due to ν(OH) indicates the presence of water. Complexes **3**, **4**, **6**, **7** and **9** show broad bands in the region 3340–3330 cm^{-1} along with the appearance of bands at 985–940 cm^{-1} (wagging modes of water) indicating thereby the presence of coordinated water [25]. Complexes **1**–**3** and **5** were heated at 115 ± 5°C for 2 h and the dehydrated complexes were analyzed for CHN and the results suggest the formation of the complexes without lattice water [Found: C 46.20; H 4.15; N 5.52; Cr 10.21, Calcd C 46.42; H 4.09; N 5.41; Cr 10.05% for the complex **1**, Found: C 46.43; H 4.18; N 8.22; Cr 10.01, Calcd C 46.51; H 4.29; N 8.14; Cr 10.07% for

Table 2. Selected infrared spectral bands of chromium(III) complexes with their tentative assignments.

	Band position								
Compound	ν(NH/OH)	ν(COOH)	ν(C=N)	ν(C–S)	ν(Cr–O)	ν(Cr–N)	ν(Cr–S)	$\nu(NH_4^+)$	Wagging mode of water
$[(H_2mcsalim)(Hmcsalim)(H_2O)Cr] \cdot 4H_2O$ (**1**)	3407(br)	1710(m)	1612(s)	719(m)	540(m)	499(m)	355(w)		
$NH_4[(H_2mcsalim)_2Cr] \cdot 4H_2O$ (**2**)	3407(br)	1715(m)	1615(s)	706(m)	541(m)	481(m)	350(w)	3081(s) 1446(s)	
$NH_4[(Hmcsalim)(SCN)_2(H_2O)Cr] \cdot 2H_2O$ (**3**)	3331(br)	1712(m)	1610(s)	705(m)	542(m)	506(m)	327(w)	3080(s) 1441(s)	961(m)
$[(H_2mcsalim)(Hmcsalim)(H_2O)Cr]$ (**4**)	3419(br)	1724(m)	1617(s)	700(m)	542(m)	495(m)	350(w)		973(m)
$NH_4[(H_2mcsalim)_2Cr] \cdot 2H_2O$ (**5**)	3406(br)	1733(m)	1635(s)	704(m)	540(m)	488(m)	345(w)	3078(s) 1440(s)	
$[(Hmcsalim)(NH_3)_2(H_2O)Cr]$ SCN (**6**)	3406(br)	1710(m)	1640(s)	703(m)	559(m)	480(m)	331(w)		961(m)
$[(Hmcsalim)(Cl)(H_2O)_2Cr]$ (**7**)	3424(br)	1735(m)	1622(s)	718(m)	538(m)	500(m)	333(w)		985(m)
$[(Hmcsalim)(CH_3COO)(H_2O)_2Cr]$ (**8**)	3418(br)	1718(m)	1626(s)	719(m)	538(m)	502(m)	347(w)		975(m)
$[(Hmcsalim)(Py)(Cl)(H_2O)Cr]$ (**9**)	3407(br)	1728(m)	1631(s)	700(m)	546(m)	496(m)	352(w)		

the complex **2**, Found: C 33.63; H 3.38; N 12.98; Cr 12.01, Calcd C 33.72; H 3.54; N 13.11; Cr 12.16% for the complex **3** and Found: C 46.53; H 4.28; N 8.09; Cr 10.16, Calcd C 46.51; H 4.29; N 8.14; Cr 10.07% for the complex **5**]. The infrared spectra of these latter complexes also showed the presence of coordinated water. The heat treatment of **4**, **6**, **7**, **8** and **9** resulted the same complexes without any loss of water molecules. The infrared spectra of these complexes showed the presence of coordinated water molecules only as indicated above.

The coordination of NH_3 in **6** is indicated by the presence of bands around 3400–3000, 1600, 1280 and 880 cm^{-1} assignable to $\nu(NH_3)$, $\delta_d(NH_3)$, $\delta_S(NH_3)$ and $\rho_r(NH_3)$, respectively [26, 27].

The presence of ammonium ion in **2**, **3** and **5** is inferred from the infrared bands in the region 3080 and 1440 cm^{-1} [28, 29]. However, due to the presence of water in these complexes the interpretation of these bands appearing in the region is very difficult.

The infrared spectrum of **3** showed bands around 2070(s) and 760 cm^{-1} (m) due to CN and C–S stretching vibrations, respectively [30–32]. The bonding of thiocyanato with chromium(III) ion occurs through nitrogen as evident from the band due to ν(C–S) at 760 cm^{-1}. Based on the data available in the literature, thiocyanato coordinates through nitrogen for first row transition metals and through sulphur for second row transition metals. The ionic nature of SCN in **6** is supported by the appearance of bands around 2045 ν(CN) and 735 cm^{-1} ν(CS).

The presence of coordinated pyridine in **9** is supported by the appearance of ν(CH) (aromatic) at ~3000 cm^{-1} and ν(C–C) (aromatic) and ν(CN) at 1440–1590 cm^{-1} [33].

It is interesting to note that in **1** and **4** two moles of the ligand are present for each molecule of the complex, one functioning as a dibasic tridentate (NSO) and the other as a monobasic bidentate (NS) (phenolic OH and carboxylic COOH remaining uncoordinated). Appearance of infrared bands at 1625 cm^{-1} (coordinated C=N), 1710 cm^{-1} (free COOH), a broad band in the region 3500–3100 cm^{-1} (uncoordinated OH) and absence of any band around 2600–2550 cm^{-1} (due to νSH) supports this interpretation. However, presence of water molecule complicates this interpretation. Therefore, in **1** and **4**, both monobasic bidentate and dibasic tridentate ligands are assumed to be present.

3.4. *Magnetic moments and electronic spectra*

All the chromium(III) complexes are paramagnetic with magnetic moment values in the range 3.78–3.89 B.M. at room temperature (table 1). These values are slightly lower than the spin-only values for a d^3 ion and this has been thoroughly discussed earlier [34, 35].

The thiazolidine ligand H_2chptz shows two intense bands around 260 and 370 nm in the DMSO solution, due to the intra-ligand charge transfer transitions [19], $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. These bands are slightly red-shifted along with other bands in the chromium(III) complexes.

The electronic absorption spectra of the isolated chromium(III) complexes synthesized in this study show bands in the range 17,035–17,241 cm^{-1} (ν_1), 22,371–22,989 cm^{-1} (ν_2), 26,315–27,100 cm^{-1} (ν_3) and 29,411–31,152 cm^{-1} (ν_4) in (DMSO) solution. All the bands are consistent with tetragonal geometry (D_{4h})

Table 3. Electronic spectral bands (cm^{-1}) and ligand field parameters.

Complex	$^4B_{1g}\rightarrow{}^4E_g{}^{(a)}$ (ν_1)	$^4B_{1g}\rightarrow{}^4B_{2g}$ (ν_2)	$^4B_{1g}\rightarrow{}^4E_g{}^{(b)}$ (ν_3)	$^4B_{1g}\rightarrow{}^4A_{1g}{}^{(b)}$ (ν_4)	B	β^0
1	17,094	22,676	27,027	29,411	683	0.75
2	17,035	22,472	26,316	29,585	681	0.74
3	17,123	22,676	26,954	306,774	685	0.75
4	17,035	22,371	26,316	30,487	681	0.74
5	17,271	22,727	27,100	31,152	691	0.75
6	17,123	22,779	26,666	29,585	685	0.75
7	17,241	22,727	27,100	30,487	690	0.75
8	17,054	22,989	26,809	29,154	682	0.74
9	17,035	22,570	26,315	30,487	681	0.74

Table 4. NSH Hamiltonian parameters.

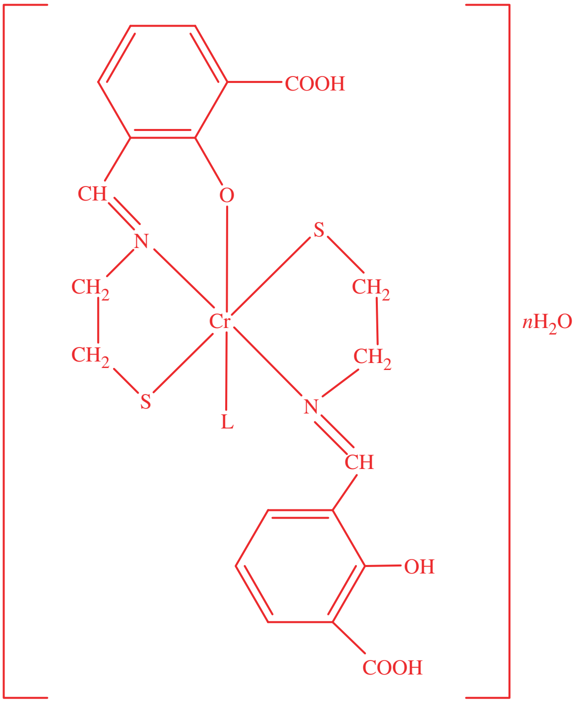
Complex	Dt	Ds	$\mathrm{Dq^{xy}}$	$\mathrm{Dq^{z}}$	DQ	DT	DS	$\mathrm{DQ^{L}}$	$\mathrm{DQ^{Z}}$	DT/DQ
1	638	−843	2268	1151	52,127	8648	5901	63,567	29,247	0.166
2	621	−851	2247	1160	51,822	8418	5955	62,958	29,550	0.162
3	635	−888	2267	1156	52,147	8608	6215	63,534	29,372	0.165
4	609	−884	2237	1171	51,740	8255	6186	62,660	29,899	0.160
5	623	−925	2272	1182	52,477	8445	6478	63,649	30,134	0.161
6	646	−848	2278	1148	52,273	8767	5937	63,871	29,078	0.168
7	626	−901	2273	1177	52,457	8486	6306	63,683	30,005	0.162
8	622	−852	2299	1226	53,236	8432	5966	64,390	30,927	0.159
9	633	−901	2257	1149	51,905	8581	6311	63,257	29,202	0.165

of the complexes. In octahedral geometry ν_1 and ν_2 may be considered as the split components of the $^4T_{2g}$ (Oh), while the bands ν_3 and ν_4 may may be considered as the split components of the $^4T_{1g}$ (F)(Oh) terms despite their high molar extinction coefficients. Similar high extinction coefficients were observed for bands of chromium(III) complexes of *N*-substituted salicylaldimines [4], *N*,*N*′-ethylene*bis*(salicylaldimine) [36] and *N*,*N*′-ethylene*bis*(acetylacetoneimine) [37].

In the absence of crystal structures of the complexes, we have calculated ligand field parameters and NSH Hamiltonian parameters (tables 3 and 4) to ascertain further the geometry of the present chromium(III) complexes. Structural correlation was demonstrated earlier [38–44]. The first spin-allowed transition $^4B_{1g}\rightarrow{}^4E_g$ gives 10 dq. The values of β^0 given in the table are similar to the earlier reported N,S bonded [42] and N,O bonded chromium(III) complexes [42].

Various NSH Hamiltonian parameters are calculated according to the method of Lever and co-workers [40] and given in table 4. The transitions of ν_2 correspond to $\mathrm{Dq^{xy}}$ and separation of ν_1 and ν_2 is 35/4 Dt, where Dt is related to the inplane and out of plane field strength via, $\mathrm{Dt} = (4/7)(\mathrm{Dq^{xy}} - \mathrm{Dq^{z}})$ [41]. The Ds and Dt values are comparable to similar chromium(III) complexes. The ratio DT/DQ of the complexes in this study lie in the range 0.160–0.168 are much lower than the limiting value (0.423) for square planer complexes suggesting small distortion from the cubic symmetry in the complexes [42].

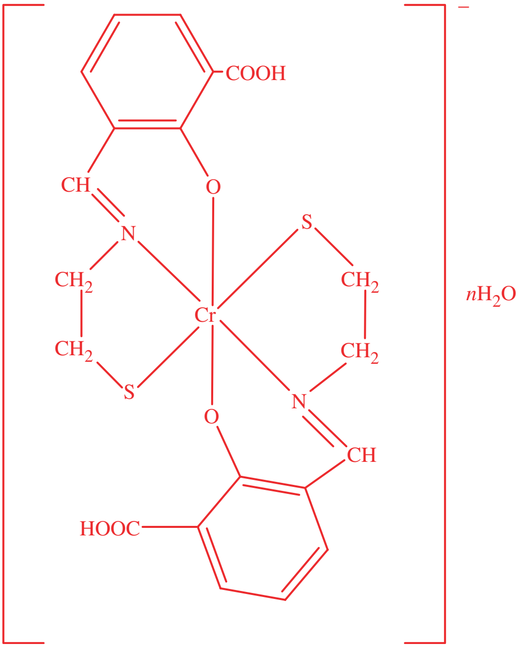
The UV spectra of all the complexes exhibit an intense absorption (with comparable intensity) in the region 35,000–38,000 cm''^{1}, which may be compared with results



1 where L = H_2O, $n = 4$

4 where L = H_2O, $n = 0$

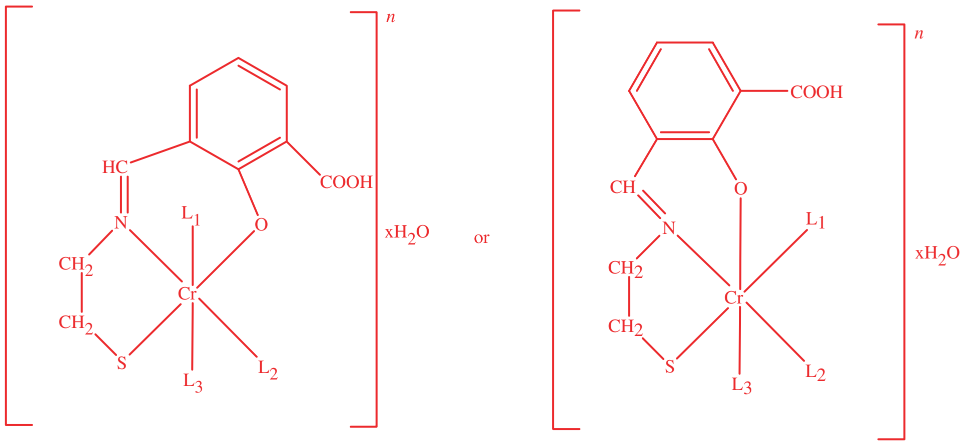
Figure 3. Proposed structures of the complexes **1** and **4**.



2 when $n = 4$

5 when $n = 2$

Figure 4. Proposed structures of the complexes **2** and **5**.



3 where $L_1 = L_2 = SCN$; $L_3 = H_2O$, $x = 2$; $n = 1^-$
6 where $L_1 = L_2 = NH_3$; $L_3 = H_2O$, $n = 1^+$
7 where $L_1 = L_2 = H_2O$; $L_3 = Cl^-$, $n = 0$
8 where $L_1 = L_2 = H_2O$; $L_3 = CH_3COO^-$, $n = 0$
9 where $L_1 = Py$; $L_2 = Cl^-$; $L_3 = H_2O$, $n = 0$

Figure 5. Proposed structures of the complexes **3** and **6**–**9**.

reported earlier for other complexes with a Cr–S bond [45]. This intense band is usually attributed to S → *Cr ligand to metal charge transfer.

Based on the above discussions, the following structures (figures 3–5) may be proposed for the isolated chromium(III) complexes.

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