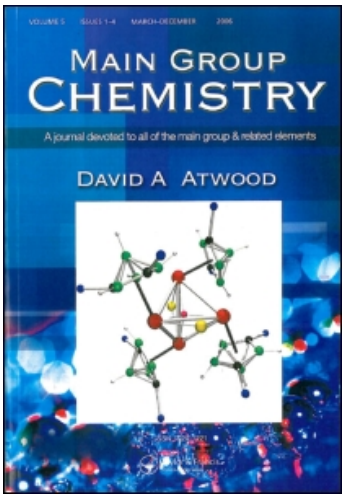

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^{1}H NMR and spectroscopic studies of biologically active yttrium (III)-flavonoid complexes

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^{1}H NMR and spectroscopic studies of biologically active yttrium (III)-flavonoid complexes

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The compounds, $Y(L1–5)_3$, [where L1–5 = quercetin (L**1**), morin (L**2**), naringenin (L**3**), catechin (L**4**) and chrysin (L**5**)] were prepared and characterized by elemental analysis, molar conductance, UV–Vis, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), and proton nuclear magnetic resonance (^{1}H NMR) spectroscopic studies. Molar conductance showed that the complexes are non-electrolytic in nature. The complexes were anhydrous as revealed by the TGA analyses. The ^{1}H NMR spectra in DMSO-d_6 revealed a diamagnetic shift. The small chemical shift of the proton resonances suggested that the complexes are dissociated in DMSO solvent and the solvent is coordinated to the Y atoms.

Keywords: yttrium; quercetin; morin; naringenin; catechin; chrysin

Introduction

Flavonoids are one of the most widespread classes of organic molecules, and are present in numerous plant tissues [1,2] and/or living organisms, and play key roles in a wide range of biological processes [3–14]. Some flavonoids possess strong antioxidant activity through their ability to scavenge free radicals and chelate metal ions [15–20]. The chelating capacities of flavonoids with metal ions such as transition and non-transition metals have been reported earlier and demonstrated that their coordination complexes were better inhibitors of free radicals than the ligands alone [17–20,21]. As a result of their potential utility in biomedical science flavonoid coordination chemistry has been extensively studied [15–25].

The yttrium (III) ion is diamagnetic and has a strong tendency to form coordination complexes with flavonoids. Moreover, the smaller size of the yttrium (III) ion may result in coordination of the relatively bulky flavonoid molecules in the inner coordination sphere of the metal.

Flavonoids possess multiple hydroxyl groups on different positions of the benzene ring. It is important to determine which hydroxyl group is deprotonated during metal coordination. This can be determined by spectroscopic studies. In this article, the synthesis, characterization and structural properties of yttrium (III) metal complexes with various flavonoid ligands (L1, L2, L3, L4 and L5) will be described. The metal complexes are isomorphous with respect to the coordination environment in the solid phase but the $Y(L1)_3$ and $Y(L2)_3$ compounds are different in solution and are seven-coordinate.

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Experimental

Materials

Yttrium oxide (99.9%, Lieco Chemicals, USA) was converted to the chloride by addition of hydrochloric acid (HCl). Quercetin dihydrate, morin dihydrate, naringenin, catechin and chrysin (99.9%, Sigma-Aldrich, USA) methanol, xylenol-orange (SD Fine Chemicals, Mumbai, India) and EDTA (BDH) were used as obtained.

Synthesis

Preparation of Y(L1)$_3$

A hot solution of 3 mmol of the L1 ligand in methanol (50 mL) was added dropwise to a stirred solution of 1 mmol of hydrated yttrium chloride in the same solvent (50 mL). The reaction mixture was stirred constantly for 6 h at 100°C temperature and the volume of the solution was reduced to produce a precipitate that was isolated by filtration and washed with chloroform. The filtrate was kept for slow evaporation at ambient temperature. The dark yellow precipitate was obtained dried under vacuum over P_4O_{10}. The synthetic method for $Y(L2)_3$ was similar but produced yellowish crystals.

Preparation of Y(L3)$_3$

Hydrated yttrium chloride (1 mol) was dissolved in 50 mL methanol mixed into the L3 ligand solution (50 mL methanol) in a 1:3 molar ratio. The two solutions were mixed thoroughly for 5 h with constant stirring on hot plate at 100°C. The volume of the solution was reduced, kept at room temperature for slow evaporation and crystallization. Dark brown needle-shaped crystals were obtained after 12 h and were collected by filtration and dried under vacuum over P_4O_{10}.

Preparation of Y(L4)$_3$

$Y(L4)_3$ was synthesized by the reaction of hydrated yttrium chloride (1 mol) with L4 (3 mol) dissolved in 50/50 mL volume in methanol with heating at approximately 100°C with stirring for 6 h. When the hot metal solution was mixed into the ligand solution a change in color was observed. The solution volume was reduced and left for slow evaporation at room temperature for crystallization. Solid brown round-shaped crystals were obtained after approximately 2 days. The crystals were isolated by filtration and dried under vacuum over P_4O_{10}.

Preparation of Y(L5)$_3$

A hot solution of L5 (3 mol) in 50 mL methanol was mixed into a hot solution of hydrated yttrium chloride (1 mmol) in 50 mL methanol and kept at a volume of 100 mL at 80°C. After stirring for one hour, yellow needle-shaped crystals formed. The crystals were filtered and washed with methanol and dried under vacuum over P_4O_{10}.

Methods or physical measurements

Microanalysis (Carbon and Hydrogen) was carried out with a FI-SONS EA-1108 elemental analyzer. The metal content of the complexes were estimated by complexometric

titration. Molar conductances of 10^{-3} M DMF solution of the complexes were measured with an orion conductivity meter. The thermograms were recorded on du Pont TA 2000 TGA machine under nitrogen atmosphere at a heating rate of 10°C per min. Melting point (MP) was measured with a Gallen kamp MBF-595 apparatus. A shimadzu UV-2501PC spectrophotometer was used to obtain the electronic spectra in the region 250–700 nm in DMF and methanol. FTIR spectra in the 4000–400 cm^{-1} regions were recorded from KBr pellets on a Perkin-Elmer Lambda-40B spectrophotometer.[1]H NMR chemical shift was measured in DMSO-d_6 on a Bruker 300 MHz spectrophotometer.

Results and discussion

The complexes were characterized using elemental analysis, molar conductance, UV–Vis, FTIR, TGA and ^{1}H NMR spectroscopic studies. The physical properties of the complexes are presented in Table 1. The data indicates that the flavonoid ligands (L1, L2, L3, L4 and L5) form bidentate chelates to the central yttrium atom (Figure 1). The syntheses were carried out in air and no precautions were taken to exclude moisture. The complexes are air stable and can be handled without any adverse effects of air or moisture. $Y(L1)_3$ is an amorphous solid, with a sharp melting point with decomposition starting after 225°C temperature. While, the $Y(L2)_3$ and $Y(L4)_3$ complexes are crystalline and they do not melt up to 300°C. However, $Y(L3)_3$ and $Y(L5)_3$ are crystalline solids and have sharp melting points at 220 and 265°C, respectively. The complexes are soluble in polar organic solvents but are insoluble in non-polar solvents. All the metal complexes have low molar conductances and are non-electrolytes in DMF (10^{-3} M) [26].

UV–Vis spectra

Electronic absorption spectra of five ligands and their corresponding yttrium (III) complexes were recorded in the range 250–700 nm in methanol and DMF (Table 2). The spectra of the free ligands were taken for comparative purpose. The spectra of the complexes were different compared with their respective ligands. There are only two absorption bands observed in the spectrum of L1 and L2 in methanol and DMF solutions (Figures 2 and 3) [16,27–29]. Two peaks at 412 (I) and 238 nm(II) in methanol, 375(I) and 262 nm (II) in DMF; at 403(I) and 236(II) in methanol, at 411(I) and 244 nm(II) in DMF are observed in the spectrum of free L1 and L2, respectively [19–22]. The observed absorption band at higher wavelength (lower frequency) is assigned to the π-π and n-π transitions, and a second band observed at lower wavelength (higher frequency) is due to

Table 1. Physical properties of yttrium-flavonoid complexes.

Complex	Color	MP°C	% Metal calculated (Observed)		
			C	H	M
$Y(L1)_3$	green	250 (dec)	54.45 (53.86)	2.74 (2.68)	8.95 (8.80)
$Y(L2)_3$	green	260 (dec)	54.45 (53.86)	2.74 (2.69)	8.95 (8.49)
$Y(L3)_3$	dark brown	220	59.87 (58.78)	3.49 (3.28)	9.84 (9.62)
$Y(L4)_3$	brown	>300	56.49 (55.89)	4.10 (3.99)	9.29 (8.79)
$Y(L5)_3$	yellow	265–70	63.69 (62.95)	3.20 (3.01)	10.47 (9.84)

*dec = decomposition.

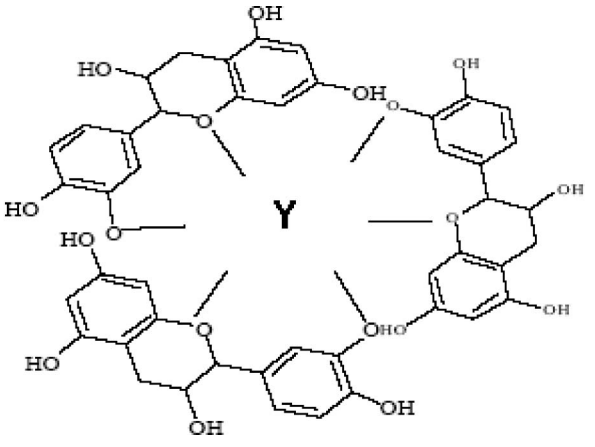


Figure 1. Proposed structure of Y(flavonoid)$_3$ complexes.

Table 2. UV/Visible spectral data of yttrium-flavonoid complexes.

Ligand/complex	L1	Y(L1)$_3$	L2	Y(L2)$_3$	L3	Y(L3)$_3$	L4	Y(L4)$_3$	L5	Y(L5)$_3$
Band I										
MeOH	412	–	403	–	278	–	261	–	–	–
DMF	375	457	411	439	284	289	282	285	315	320
Band II										
MeOH	238	–	236	–	246	–	240	–	–	–
DMF	262	370	244	360	259	258	–*	254	269	280
Band III										
MeOH	–	262	–	285	–	–	–	–	–	–

the π-π and n-σ transitions, that correspond to ring A (quinolic system) and ring B (catechol system), respectively [28,29]. The complexes spectra in DMF revealed three bands, I at 457, II at 370 and III at 262 nm; I at 439, II at 360 and III at 285 nm are observed in in Y(L1)$_3$ and Y(L2)$_3$ complexes, respectively (Figures 1–3). The shift of the absorption bands with respect to the ligand towards higher wavelength clearly indicates that ring A is associated with the metal ion. An extra band with high intensity is also observed in the middle of these two bands. Perhaps the presence of this extra band indicates that the solvent is involved in coordination to the metal ion. Generally, a difference in the absorption spectra indicates a difference in the environments of the metal ion, but the change in band shapes, change in the intensity and shift of bands towards higher wavelength (red shift) with an extra band, which are measured in the spectrum of complexes, which is due to the solvent, offer some measure of the relative coordinating ability to the metal ion. As shown in Figures 2 and 3, the change in the spectra of the complexes demonstrates a change in the environment of the metal ion, for which a reasonable explanation is that the solvent coordinated with the metal ion causes a change in symmetry of the field and effective geometry. Iftikhar and his coworkers [30–32] have reported that DMF is especially effective in coordination, which has a high Gutmann donor number [33], enters the inner coordination sphere of the yttrium (III) complexes without replacing any ligand molecule(s). That DMF is not displacing the ligands is shown

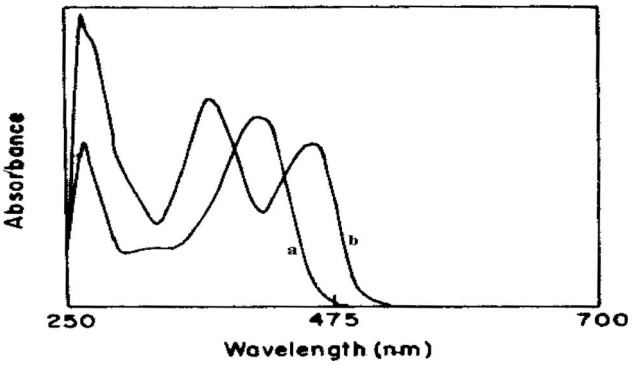


Figure 2. Absorption spectra of (a) L1 and (b) $Y(L1)_3$ in DMSO.

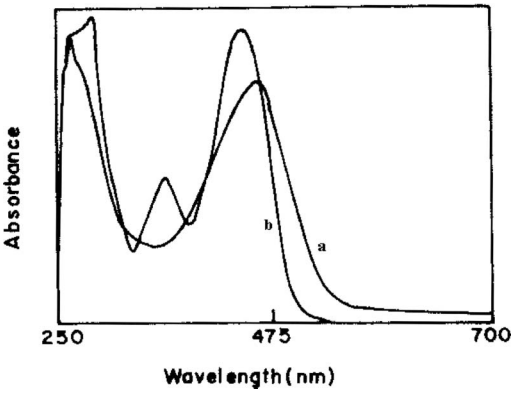


Figure 3. Absorption spectrum of (a) L2 and (b) $Y(L2)_3$ in DMSO.

in the non-electrolytic nature of the molar conductance [26]. It is strong evidence that DMF is associated to the metal ion. Therefore, DMF solvent is coordinated to the metal ion and increases the coordination number of the metal complexes from six to seven. Unfortunately, the number of DMF molecules involved in coordination is not known with certainty due to the presence of similar species for both of the systems (L1 and L2).

The absorption spectrum of L3, L4 and L5 and their respective complexes in methanol and DMF solvents exhibited only two transitions between 250–700 nm regions. Band I is related to ring A and band II to ring B in these ligands spectrum (Figure 4) [28,29]. After complexation band I was shifted at lower energy (higher wavelength) in comparison to the ligand, and it was suggested that metal is coordinated to ring A in the complexes. The bands in the spectrum of complexes exhibited small red shift in respect to their free ligand spectrum. Perhaps, it is concluded that the complexes are dissociating in the nitrogen donor solvent (DMF), due to DMF high Gutmann donor number and showed strong affinity to the metal ion. There is no change in the coordination number of the complexes in solid phase and solution medium. Thus, on the above explanation, it is proposed that $Y(L1)_3$ and $Y(L2)_3$ are seven coordinate, whereas $Y(L3)_3$, $Y(L4)_3$ and $Y(L5)_3$ are six coordinate in DMF solution.

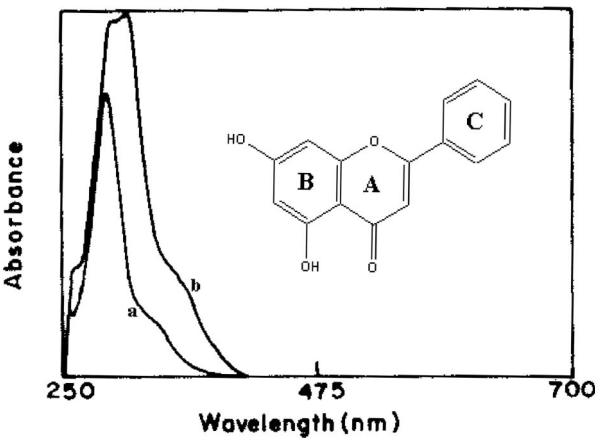


Figure 4. Absorption spectra of (a) L5 and (b) $Y(L5)_3$ in DMSO (inset shows the molecular structure of chrysin).

Infrared spectra

Infrared absorption frequencies of free ligands and their respective yttrium (III) complexes with tentative assignments are summarized in Table 3. The vibrational spectral data of the ligands and their complexes are in accordance with the structure. On comparing the spectra of ligands with their respective complexes, important distinctions are revealed. A small peak is observed at lower wave number between 520–488 cm^{-1} in all complexes, which is not measured in the free ligand spectrum. The presence of this band indicates metal–oxygen bonding [34,35].

A diffuse band appears in the spectra of the free ligands and complexes in the region 3500–3000 cm^{-1}. This corresponds to the ν(O—H) frequency [34–36]. This band in the spectra of L3, L4 and L5, is very broad and may be due to hydrogen bonding between the ketonic and hydroxyl groups. This band is attributed to the coordination of ligand to the metal ion and breaking of the intra- and intermolecular hydrogen bonding after complexation. In the free ligand spectra two moderate sharp intensity bands are observed at lower wave numbers in the range 1000–750 cm^{-1}. These bands are attributed to the ν_r(O—H) and ν_w(O—H) frequencies of O—H groups in the ligands [34,35]. The bands are shifted to lower wavenumber with more moderate intensities than the ligand spectra. The appearance of this band may be due to water absorption by the complexes.

A strong band in the range 1666–1600 cm^{-1} is observed, that corresponds to νC=O stretching vibrations, but this band is not revealed in the L4 spectrum due to the absence of a ketonic group in the ligand. The ν(C=O) stretching vibration frequency in the complexes decreased by comparison to the ligand spectra. A decrease in this frequency indicates that the carbonyl group is involved in coordination. The characteristic ν(C—O—C) anti-symmetric and symmetric stretching vibrations of the ligand measured between 1382–1285 cm^{-1} are not changed significantly and suggests that this group does not form metal-oxygen bonds in the L1, L5 and L3 complexes [20,22]. In the case of the L4 and L2 complexes, the shifts of the stretching ν(C—O—C) frequency moves higher than the ν(C=O) frequency. This reveals that the ligands are coordinating through this site. In the spectral region of 1600–1250 cm^{-1}, the ν(C—O), ν(C—C) stretching and (C—H) bending vibrational modes from biphenolic and quinolic rings dominate, yielding peaks with contribution from both (C—O), (C—C) and (O—H) bending modes. The skeletal ring

Table 3. IR absorption frequencies of yttrium-flavonoid complexes.

Functional groups	L1	Y $(L1)_3$	L2	Y $(L2)_3$	L3	Y $(L3)_3$	L4	Y $(L4)_3$	L5	Y $(L5)_3$
ν(O−H)	3409–3100	3360	3479–3000	3361	3400–3112	3291	3341	3356	3400–3100	3088
ν(C−H)	2965	2930	2927	2932	2919, 2831	2922	2926	2900	2926	2927, 2716
ν(C=O)	1666	1618	1653	1629	1631	1604	–	–	1653	1647
ν(C=C)	1611, 1562, 1522	1516	1607, 1572, 1509	1512	1602, 1519, 1497	1508	1629, 1607, 1521	1625, 1517	1611, 1576, 1553	1493
δ(O−H) C−O−H	1452	1429	1450	1441	1421	1464	1460	1457	1450	1456
ν(C−O) C−O−C, C−C−O	1382, 1320	1359, 1317	1352, 1327	1363	1388, 1338	1390, 1312	1373, 1285	1370	1356, 1313	1358
ν(C−C) C−C−C ‖ O	1262	1212	1309, 1246	1234, 1177	1312	1251	1239	1278	1245	1166
ρ (O−H) in plane	1014	1164	1203	1101	1249	1161	1146	1143	1168	1028
(C−H) in plane	1199, 1169	1096	1173, 1089	1009, 975	1179, 1156	1075	1111, 1079	1030	1029	907
(C−C) in plane	864	1005, 933	1006, 975	834, 800	1082, 1063	1015, 970	1030	874	907	841, 803
(O−H) out of plane	822	883	828	693	832	833	822	817	841	735
(C−H) out of plane	722	812	703, 686	646	729, 666	760, 726	765	766	806, 782, 731	685
(C−C) out of plane	679, 602	696, 597	638, 568	576	630, 612	618, 666, 558	669	623	692, 641	642
M−O	–	488	–	500	–	492	–	520	–	507

bands (−C−C−) frequency are observed as doublets. The region 1250–1000 cm^{-1} is characteristic for the (O−H), (C−H) and (C−C) in-plane bending modes of the aromatic benzene rings; except some exceptions due to the strong coordination of ligand to the metal ion and decrease in length with increase in its wave number. In the 1000–600 cm^{-1} spectral region the bands are attributed to the δ(C−H), δ(O−H) and δ(C−C) out-of-plane ring vibrational modes. This is also supported in the UV–Vis spectral results, where ring A (quinolic system) revealed coordination to the metal ion [36].

Thermal analysis

The thermograms of the yttrium complexes are recorded from ambient temperature to 600°C. The thermal data are summarized in Table 4. The main objectives of the thermal analysis are to assign the number and nature of water molecule(s) present in the complexes. All the yttrium-flavonoid complexes are anhydrous in nature and do not show

any weight loss up to 200°C. The thermograms of L1 and L2 complexes are similar in nature, may be due to both are analogous geometrically. First derivative curve is observed at 325 and 323°C temperature with the weight loss 28.65 and 29.74% in L1 and L2 complex spectrum, respectively. This weight loss is equivalent to one molecule of L1/L2 (cal. wt. loss for one molecule of L1/L2 is 30.42%). In the second decomposition step, a second molecule of L1/L2 is eliminated and followed by a third molecule of the complex. Before complete removal of second molecule the third molecule begins to eliminate out which is reflected by a TGA break and a DTG peak at 451 and 434°C. The observed weight loss at this temperature is 63.50 and 60.45% for two molecules of L1/L2, respectively (cal. wt. loss for two molecules of L1/L2 is 60.84%).

Table 4. Thermal analysis data of Y(flavonoid)$_3$ complexes.

Complexes	Temperature (°C)	Weight loss (%)		Constituents eliminated
		Calculated	Observed	
Y $(L1)_3$	325	30.42	28.65	One molecule of L1
	451	60.84	63.50	Two molecules of L1
Y $(L2)_3$	323	30.42	28.74	One molecule of L2
	434	60.84	60.45	Two molecules of L2
Y $(L3)_3$	264	30.13	29.50	I molecule of L3
	335	30.13	25.58	II molecule of L3
	439	30.13	20.00	III molecule of L3
Y $(L4)_3$	318	30.23	30.00	I molecule of L4
	387	30.23	24.85	II molecule of L4
	432	30.23	26.45	III molecule of L4
Y $(L5)_3$	295	59.86	58.25	Two molecules of L5
	359	29.93	28.50	One molecule of L5

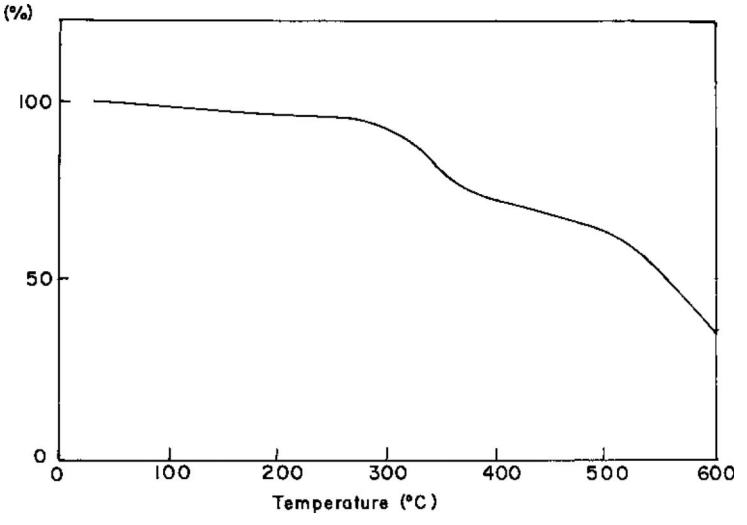


Figure 5. TGA spectrum of Y(L5)$_3$.

Table 5. ^{1}H NMR spectral analysis of yttrium complexes with flavonoids.

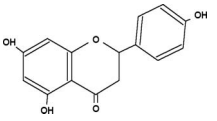
	Chemical shifts										
Complex/ Ligand	5-OH	7-OH	3-OH	4′-OH	3′-OH	H-2′	H-6′	H-5′	H-8	H-6	H_2O
(a) L1 complex											
L1*	12.52[a]	10.80	9.58	9.32	9.29	7.65	6.92	6.51	6.83	6.16	3.3–4.0
$Y(L1)_3$	12.47	10.88	–	9.63	9.33	7.66s	7.55d	6.90d	6.43s	6.20s	–

[a]For references, 16,17 & 22.

(b) L2 complex

Complex/ Ligand	5-OH	7-OH	3-OH	4′-OH	2′-OH	H-6′	H-5′	H-8	H-3′	H-6	H_2O
L2	12.62[a]	10.55	9.78	–	–	7.07	6.28	6.20	6.15	6.05	3.0–3.7
$Y(L2)_3$	12.60	11.40	9.85	10.82	–	8.06d	6.95d	7.56s	6.39s	7.23s	–

[a,b]For reference 20.



structure of naringenin

(c) L3 complex

Complex/ Ligand	5-OH	7-OH	4′-OH	H-3′&5′	H-2′&6′	H-6	H-8	H-2	H-3
	–	–	–	7.23d[a]	6.74d	5.80s	5.26d	3.03t	2.72d
L3	12.06	10.75	9.54	7.25d	6.72d	5.80s	5.38d	3.13	2.63d
$Y(L3)_3$	–	10.47	9.36	7.28d	6.82d	5.89s	5.36d	3.11t	2.72d

[a]Chemical shifts measured in CD_3OD-d_4.

(d) L4 complex

Complex/ Ligand	5-OH	7-OH	4′-OH	3′-OH	3-OH	H-2′	H-4	H-6	H-8	H-5′	H-6′	H-2	H-3
L4	–	–	–	–	–	6.84[a]	6.75	5.86	5.93	4.58	4.55	6.78	3.99
	9.17	8.94	8.85	8.81	not obs	6.67s	6.72d	5.69s	5.89s	4.49d	4.87d	6.61d	3.83m
$Y(L4)_3$	9.20	8.96	8.87	–	not obs	6.67s	6.72d	5.69s	5.89s	4.48d	4.88d	6.60d	3.81m

[a]Chemical shifts measured in CD_3OD-d_4.

(e) L5 complex

Complex/ Ligand	5-OH	7-OH	H-2′&6′	H-3′&5′	H-3	H-8	H-6
L5	12.82s	10.92s	8.04–8.14	7.36–7.62m	6.97s	6.53d	6.22d
$Y(L5)_3$	notobs	10.94	8.31d	7.64m	6.98s	6.54	6.24

Chemical shifts are expressed in ppm (δ); s: singlet; d: doublet; m: multiplet.

The thermogram of $Y(L3)_3$ shows the first TG curve at 264°C with a weight loss of 29.55% which is equivalent to one molecule of L3 (calc. wt. loss for one unit of L3 is 30.13%). Two inflexion points are observed at the temperature 335 and 439°C with the observed weight losses of 25.58 and 20.34%, which represents the expulsion of both units of L3. The observed weight loss at this temperature is less than the required weight loss for one molecule of L3. This is because even before complete expulsion of second molecule of L3, removal of third molecule begins, which is reflected by a TGA break and a DTG peak at these temperatures.

The thermogram of $Y(L4)_3$ shows three stepwise decomposition in TGA spectrum. First inflexion point in the thermogram of the complex revealed at 318°C temperature, with weight loss 30%, for one molecule of L4 (calc. wt. loss is 30.23%). After elimination of the first molecule of L4 decomposition of second molecule is started and TGA curve is observed at 387°C, with weight loss 24.85% (calc. wt. loss for second molecule is 30.23%), without complete expulsion of second molecule the decomposition of third molecule of L4 is started to come out at the temperature 432°C, with the weight loss 26.45% (calc. wt. loss 30.23%). The TGA spectrum shows a peak at this temperature.

The thermogram of $Y(L5)_3$ exhibits first inflexion point at 295°C in the TGA curve, with a weight loss of 59.25% and a corresponding DTG peak at this temperature (Figure 5). This weight loss is equivalent to the loss of two molecules of L5 (calc. wt. loss for two molecules of L5 is 59.86%). The second inflexion point observed in the TGA spectrum of $Y(L5)_3$ at 359°C, shows a weight loss of 28.50% and represents elimination of a third molecule of L5 (calc. wt. loss for one molecule of L5 is 29.93%) (Table 4).

NMR spectra

^{1}H NMR spectra of ligands and their respective yttrium complexes are recorded in DMSO-d_6 solvents. The spectral data of ligands and their respective complexes with their tentative assignments are summarized in Table 5(a)–(e). The aromatic ring proton resonances of the flavonoids revealed downfield as well as upfield chemical shifts in the spectra of yttrium-flavonoid complexes (Figures 6–8). The upfield shift of proton resonances in the complex spectra is due to an increase in the ring current shielding effect

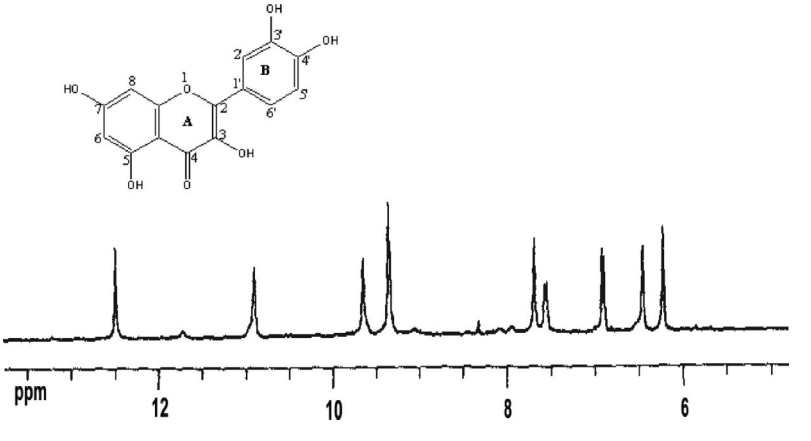


Figure 6. ^{1}H NMR spectrum of $Y(L1)_3$ (inset shows the molecular structure of quercetin).

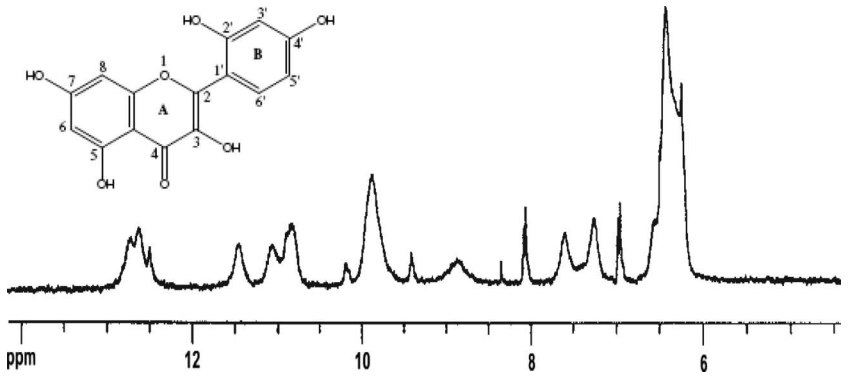


Figure 7. ^{1}H NMR spectrum of $Y(L2)_3$ (inset shows the molecular structure of morin).

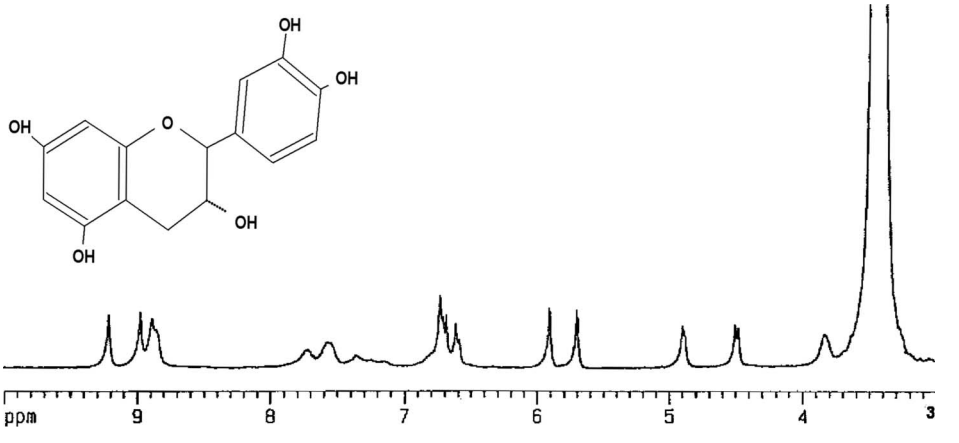


Figure 8. ^{1}H NMR spectra of $Y(L4)_3$ (inset shows the molecular structure of catechin).

after complexation [Table 5(a)–(c)]. The higher field shift can be explained by the extension of the conjugated system with the complexation. Therefore, the proton is more shielded and the signal is shifted to higher field [37]. On comparing the NMR spectra of the complexes with their corresponding ligands the signals of the hydroxyl protons of 3-OH, 2′-OH, 5-OH, 5-OH and 7-OH groups of L1, L2, L5, L3 and L4 complexes, respectively, were not observed [Table 5(a)–(e)]. This indicates that this group loses the proton during the bonding of ligand to the metal ion in the complexes (Figures 6–8). A larger downfield shift was detected for H-8 in the L2 complex because it is closer to the coordinating (C—O—C) group [Figure 6, Table 5(b)]. The greater downfield shift of this proton resonance confirms the stronger binding of this group. Perhaps the small chemical shifts of L5 proton resonances in the complex spectrum in DMSO-d_6 solution indicate that the complex is dissociated in this solvent [Table 5(e)]. This fact also confirmed from the absorption spectrum result of this complex and reported data, which (DMSO) have a very high Gutmann donor number [33]. These results were agreed to the UV–Vis spectral

results, which showed that the solution spectrums of complexes were unaffected and no changes were observed with respect to their ligands.

Conclusions

The flavonoid ligands are isostructural but show different coordination geometries around the metal ion. The results of spectral studies (^{1}H NMR, FTIR, TGA and UV–Vis) provide coordination behavior of ligands and their geometrical structures. On the basis of spectral results it is proposed that $Y(L1)_3$ and $Y(L2)_3$ are seven coordinate, whereas $Y(L3)_3$, $Y(L4)_3$ and $Y(L5)_3$ are six coordinate in DMF solution. The absence of water molecule in the coordination sphere was confirmed by TGA. The spectroscopic data demonstrated the coordination behavior of these complexes which are heavily influenced by the binding of flavonoid ligands.

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